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A FINAL TECHNICAL REPORT

TO

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TITLE   Adsorption of Humic Acids and Trace Metals
                         in Natural Waters

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ABSTRACT

Studies concerning the interactions between suspended hydrous iron oxide and dissolved humic acids and trace metals are reported. As a major component of dissolved organic matters and its readiness for adsorption at the solid/ water interface, humic acids may play a very important role in the organo-metallic geochemistry of suspended sediments and in determining the fate and distribution of trace metals, pesticides and anions in natural water systems.

Most of the solid phases in natural waters contain oxides and hydroxides. The most simple promising theory to describe the interactions of hydrous iron oxide interface is the surface complex formation model. In this model, the adsorptions of humic acids on hydrous iron oxide may be interpreted as complex formation of the organic bases (humic acid oxyanions, RO_x^{-z}) with surface Fe ions. Measurements on adsorptions were made in both fresh water and seawater. Attempts have been made to fit our data to Langmuir adsorption isotherm. Adsorption equilibrim constants, K_i, were determined.

INTRODUCTION

The presence of suspended particles in natural waters has a significant influence over the chemical composition of the whole system. The objective of our research project is to study the interactions between suspended particles and dissolved organic matters such as humic acids and trace metals.

Suspended solids are introduced into the natural bodies of water by natural forces, e.g. weathering, volcanic emanation, or by man-made activities, e.g. sewage discharge, dredging, continental drilling, ... Regardless of their sources and origins, suspended solids can be classified as inorganic oxides (quartz, ferric oxides, Al_2O_3), carbc·ates, clays, and as organic detritus (organic colloidal matter of detrital origin), as well as living micro-organisms-algae and bacteria. The importance of suspended particles lies in their unique characters, specially small size, large specific surface area, and charge-carrying in the aqueous system. Solids in natural waters have electrically charged surfaces. Near neutral pH value, clay, most insoluble oxides, organic pollutants, bacteria and algae are characterized by a negative surface potential as indicated by negative values of the electrphoretic mobility.[1-4]

It is generally known that solutes tend to accumulate at the solid-solution interface. The concentration of chemical species, such as trace metals, hydrocarbon, phosphate and silicate in the bottom sediments or in the particulate solids of aqueous system is at least one or more orders of magnitude larger than that found in the solution part. The absorption characteristics of soluble chemicals, e.g. trace metals, pesticides, and inorganic anions onto various solids, e.g. oxides, carconates, clays, soils, and organic detritus exactly reflect the importance of solid-solution interface and its role in controlling the chemical composition of the natural waters. All available information indicates that pH, the chemical composition, and crystal structure of the solid and the concentration of adsorbate govern significantly the

adsorption of metal ions at the solid-solution interface. A significant fraction of trace metals in water and sediment phase is often associated with organic matters such as humic substances (of the humic acia and fulvic acid type). Humic substances are highly oxidized and chemically and biologically stable polymeric compounds which have reported molecular weights in the range of several hundred to several million and carry carboxyl and hydroxyl functional groups.[5] As a major component of dissolved organic matters and its readiness for adsorption at the solid/water interface, humic acids may play a very important role in the organo-metallic geochemistry of suspended sediments and in determining the fate and distribution of trace metals, pesticides and anions in natural water systems.

Most of the solid phases in natural waters contain oxides or hydroxides. Various theories have been proposed to describe the absorption of ions at hydrous oxide interface. But the most simple and promising one is the surface complex formation model.[6-7] In this model the hydrolysis of oxide surface produces hydrous oxide surface groups as $\equiv Si-OH$, $\geq Mn-OH$ and $>Fe-OH$. The surface hydroxyl groups have amphoteric properties. Protonation or deprotonation resutls in surface charge on the oxide surfaces, e.g. $\geq MeOH_2^+ \rightleftharpoons \geq MeOH + H^+$ $\geq MeOH \rightleftharpoons \geq MeO^- + H^+$ where Me = metal (e.g. Fe, Mn, Si, Al) of solid oxides.

The pH of the solution is the parameter which determines the surface charge and potential of the oxides; and this solution property provides the mechanism through which the coulombic interactions between the ions and the surface may be controlled. The pH at which $(MeOH_2^+)$ = (MeO^-) is called the pH of zero point of charge pH_{ZPC}. For example, pH_{ZPC} of Goethite (α-FeeOOH) ranges from 7.5 to 8.3 in NaCl solution;[8] at oceanic pH of 8, the demination surface species is (FeOH).

Because of the pH-dependent charge characteristics, these oxides can exhibit either cation or anion exchange characteristics, dependent upon pH. But in

addition to their purely electrostatic effects on the ionic solutes, hydrous

oxides show a strong tendency to interact chemically with anions as well as

cations. These chemical interactions may be explained most satisfactorily

in terms of complex formation. For example, the interactions with anions can

be interpreted as a ligand exchange, $\geqslant$Me-OH + $HPO_4^{2-} \longrightarrow$ $\geqslant$Me-OPO$_3$H$^-$ + OH$^-$, and

those with cations as a coordination with electron acceptors $\geqslant$Me-OH + Cd$^{2+} \longrightarrow$

$\geqslant$Me-OCd$^+$ + H$^+$. In the natural water environment γ-Al$_2$O$_3$ and goethite [9] are

mostly responsible for the removal of Cd(II) and Zn(II).

During the past year we have made a number of measurements on the adsorp-

tion of humic acids on hydrous iron oxide mainly in fresh water and in seawater

as well. The results of such adsorption experiments   presented at the

American Chemical Society's 34th Annual Southeastern Regional Meeting, Birming-

ham, Alabama, 1982, are shown in Figures 1-20 and Tables 1-20.

Athough attempts have been made to prepare the same suspensions for ad-

sorption studies from reagent solutions of the same concentrations, the results

of such studies are very difficult to reproduce. The methods (such as rate of

mixing, stirring, etc.) used to mix solutions for the preparation of these

suspensions often influence the course of the subsequent precipitation, and so

the availability of active sites on the solid surface as well as the size of the

suspended particle. For these reasons, a seed suspension technique was adopted

for some adsorption experiments so that we may be able to use the same kind of

suspension for reproducible studies. The effects of factors such as ionic

strength, temperature, pH and additives may be studied quantitatively. Also

the influence of particle morphology may be investigated.

Undergraduate students were involved in this project to learn general

techniques and the application of these techniques to the studies of adsorption

in particular. As a result, the students have been familiar with (a) the use

of atomic absorption spectrophotometry (AAS) for the analysis of trace metals;

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(b) UV/visible spectrohotometer for the measurement of humic acids; (c) the performance of liquid scintillation counting techniques; (d) the separation of suspensions; and (e) the calculations and the principles of the interactions at the solid/liquid interface.

EXPERIMENTAL

Adsorption experiments were designed to demonstrate under conditions similar to those in the natural water environments, the interactions of suspended particles with humic acids and the effect of adsorbed humic acids on trace metal uptake.

During some studies of adsorption in seawater, we used artificial rather than natural seawater to minimize biological effects and to provide a reproducible solution of known composition. The artificial seawater was prepared by the formula of Kester, et al.[10]

Preparation of Solids (Adsorbents)

Amorphous iron oxide was prepared by slowly adding NaOH (2.5 m) to a vigorously stirred ferric nitrate solution until a pH of 8.0 was reached. NaOH to $Fe(NO_3)_3$ was at an OH:FE ratio of three. The precipitate was aged before beginning adsorption experiments. In order to obtain fresh precipitate, the suspension from mixing NaOH and $Fe(NO_3)_3$ was simply diluted with water (or artificial seawater) to give concentration in the desired range. 0.005 M $Fe(NO_3)_3$ was used for the preparations of suspensions and was freshly prepared each time.

Since such experiments were very difficult to reproduce, a study was made of the adsorption of humic acids using a reproducible seed technique. Three preparations of seed suspensions of hydrous iron oxide were used. They were all prepared by adding 2.5 M NaOH solution to 0.005 M $Fe(NO_3)_3$ solution,

washed several times and aged. Seed suspension I was prepared by slowly adding dilute NaOH solution to 0.005 M Fe $(NO_3)_3$ with constant stirring. Seed suspension III was prepared by slowly (drop-wise) adding 2.5 M NaOH solution to 0.005 M Fe $(NO_3)_3$ without much stirring. Seed suspension V was prepared by quickly adding 2.5 M NaOH solution to 0.005 M Fe$(NO_3)_3$ with constant stirring. They were of mean size of about 5 μm.

Adsorption Analysis

The adsorption experiments were carried out in the suspensions of hydrous iron oxide of approximately 50 mg per liter. Humic acid was added to achieve the desired initial solute concentration. The mixture was shaken in stoppered bottles on an automatic shaker for 24 hours to equilibrate the adsorption system. The suspended particles were then isolated by filtration (pore size 0.45 μm). The concentrations of humic acids remaining in the aliquots were analyzed by a spectrophotometer. Spectronic 21 (Bausch & Lomb). The adsorbances of the resulting solutions were measured at 365 nm. PA-720 HIAC Particle Size Analyzer was used to measure the size distribution of particular matters.

RESULTS AND DISCUSSION

The results have illustrated the effect of temperature, aging, and size and effective surface area on the adsorption behavior of humic acids on hydrous iron oxide. From Figure 1 and Table 1, it appears that 90% adsorption took place in the first 2 hours, equilibrium was reached after 20 hours of shaking and remained so to 48 hours. Criteria for attainment of equilibria in adsorption (or reactions) at hydrated solid surfaces are often difficult to establish. After the initially rapid adsorption, ferric oxide surfaces continue to adsorb humic acids very slowly. The slow adsorption (or reactions) may arise from the structure rearrangement of oxide surface to expose effectively a greater number

of FeOH sites at the interface.

The results as illustrated in Figure 1 show that adsorption of humic acids decreased rapidly with rising temperature. From the thermodynamic point of view, all adsorption processes are exothermic (i.e., ΔH must be negative), the extent of adsorption, therefore, decreases with increasing temperature.

The effects of aging hydrous iron oxide by allowing the suspensions to stand at room temperature for several weeks before adsorption experiments were studied. The results obtained showing a definite decrease in humic acids adsorption are presented in Figure 1 and Table 18. The aging effects appears very pronounced and cannot be ignored. The size relationship observation in Table 19 serves to demonstrate surface area control of humic acid adsorption, which were usually overlooked.

The adsorption of humic acids on hydrous iron oxide may be interpreted as complex formations of the organic bases (humic acid oxyanion, RO_x^{-z}) with surface Fe ions. This is consistent with a mechanism involving ligand exchange of humic anion groups with H_2O and OH^- of surface $Fe-OH_2^+$ and FeOH groups respectively. The adsorption of humic acids on hydrous iron oxide (and other suspended particles as well) is likely to modify substantially their surface properties in aqueous systems. The reaction between the oxyanions of humic acids and Fe of iron oxide surface is given

$$)Fe-OH + RO_x^{-z} \; \rightleftharpoons \;)Fe-ORO_{x-1}^{1-z} + OH^-$$
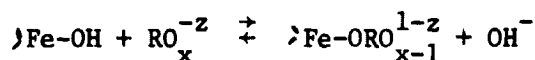
The bond strength between Fe and the O of oxyanion may be positively related to the logarithm of the complex formation constant K_1 where

$$K_1 = [Fe-ORO_{x-1}^{3-z}] / ([Fe^{3+}(aq)][RO_x^{-z}])$$

for a reaction.

$$Fe^{3+}(aq) + OR_x^{-z} \; \rightleftharpoons \; Fe-ORO_{x-1}^{3-z}$$
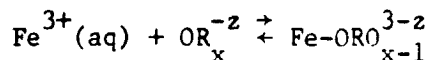
However the complex formation constant, K_1 is not yet known.

Adsorption is most often described in terms of isotherms which show the relationship between the quantity of solute adsorbed on suspended particles and bulk activity (concentration, C) at a given temperature. Attempts have been made to fit our data to the Langmuir adsorption isotherm. Let the surface equilibrium for adsorption process be represented by the equation

$$1-\theta + C_f \underset{\leftarrow}{\overset{K_1}{\rightarrow}} \theta$$

where C_f is the equilibrium concentration of adsorbate, $\theta = \Gamma/\Gamma_m$, the fractional coverage of surface sites; Γ is the adsorption density (adsorbed quantity) in mg per gram of suspended particles. Γ_m is the adsorption density for monolayer; K_1 is the adsorption equilibrium constant related to the free energy of adsorption, ΔG_{ads} by

$$K_1 = \exp(-\Delta G^o_{ads}/RT)$$

$$K_1 = \frac{\theta}{(1-\theta)C_f} = \frac{\Gamma/\Gamma_m}{(1-\Gamma/\Gamma_m)C_f}$$

$$\Gamma = \frac{\Gamma_m K_1 C_f}{1 + K_1 C_f}$$

The above Langmuir isotherm equation can be arranged into a linear form, thus

$$\Gamma = \Gamma_m - (\frac{1}{K_1}) \frac{\Gamma}{C_f}$$

The adsorption isotherms were determined by plotting (1) Γ versus C_f to show the change of adsorption (surface coverage) with free humic acids concentration. The results are given in Figures 2-4,8,11,13,15,17,19, and (2) Γ versus Γ/C_f gives a straight line with the slope of $1/K_1$ and the intercept of Γ_m, as shown in Figures 5-7,9,10,12,14,16,18,20. The values of adsorption capacity

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Γ_m (monolayer) and K_i (adorption equilibrium constant) are summarized in Table 20. The results show good fits to the Langmuir isotherm.

From the experiment F1, F2 and F3 in which the suspensions were prepared under similar conditions, the parameters $K_i = \exp[-\Delta G^o_{ads}/RT]$ appear to be closely the same. But the adsorption capacity, Γ_m (the number of available sites) are different from different suspensions. It may be that the reason for the different values of Γ_m is simply the size of suspended particles.

The most notable criticism of the Langmuir adsorption equation concerns the simplifying assumption that the free energy of adsorption ΔG_{ads}, is independent of surface coverage (Θ); solid surfaces tend to be non-uniform in nature. In our experiments, since the pH of the suspension during adsorption remained at about 8 ($\pm$ 0.5), the proportions of $Fe\text{-}OH_2^+$, $Fe\text{-}OH$ and FeO^- of the surface should remain about the same. In other words, the oxide surface remain in a similar environment, although the available adsorption sites decrease on adsorption. This may explain why K_i as a measure of the affinity of the surface of humic acids is more or less the same in experiments F1, F2, and F3 and so Langmuir equation is observed.

The results of the adsorption studies of Cd^{2+} on hydrous iron oxide are given in Figure 21 and Tables 21, 22, and 23. A nearly linear increase of adsorption either in fresh water or in seawater was observed over the range of free Cd^{2+} ion concentration from zero to 12 µg per liter (when equilibrium was reached). The evidence indicates that Cd^{2+} ion was readily adsorbed by hydrous iron oxide at the value of pH equal 8. With the concentration of Cd^{2+} we used in this study, the adsorption capacity (Γ_m) of hydrous iron oxide for Cd^{2+}ion was far from being reached since the limiting plateau of adsorption isotherms was out of sight. Results from the present study confirm the observation in literature[11] that dissolved trace metal concentrations in rivers are low and most likely non-problematic because more than 90% of the metal load of the river is associated

with particulate matter.

The effect of ionic strength on the adsorption was well demonstrated in Figure 21; the adsorption for Cd^{2+} was very much decreased in the medium of seawater. The ionic strength controls the charge density in the diffuse double layer. When the ionic strength is increased, at constant pH, the electrical double layer around the particle is compressed. The electric field ($d\psi/dx$), at a given point, is increased, thus resulting in higher solvation energy contributions to the free energy of the adsorption process. The coulombic energy is also decreased, although the coulombic energy is minimized in hydrous iron oxide suspensions at pH equal 8. As a result, the adsorption of Cd^{2+} is reduced.

However, the solvation energy (as well as coulombic energy) decreases with increasing ionic dimensions. Thus, for humic acids because of large size of oxyanion, the increase of ionic strength becomes a favorable effect on the adsorption process as illustrated in Figure 15.

Since pH of Goethite (α-FeOH) ranges from 7.5 to 8.3 (Balistrieri and Murray, 1979)[8], it is reasonable to assume that the specific interaction component (non-electrostatic) is the major contribution to the change of the Gibbs free energy, ΔG_{ads}, during the adsorption on hydrous iron oxide. More adsorption experiments will be needed to illustrate possible mechanism. In addition to hydrous iron oxide, sediments collected from adjacent rivers may be used as an adsorbent in further study.

CONCLUSION

We present the results of adsorption experiments with humic acids and trace metal (Cd) using hydrous iron oxide as a model adsorbent for natural water systems. Although the concentrations of hydrous iron oxide are higher than normally would be encountered, the experimental conditions reflect the concentrations of humic acids (as dissolved organic carbon) and Cd^{2+} possibly found in

natural waters. The pH of all the reaction media was adjusted to 8.0, which closely represents the pH conditions of seawater.

Although the exact mechanism of surface bonding remains unknown, it is apparent that humic acids complexes are present at the surface. Since adsorbed humic acids possibly have functional goups directed toward solution, these ligands may serve as complexing agents at the surface. Humic acids coated on surface oxide may help control the distribution of trace metals in natural waters by binding through complexation with coated humic acids rather than reactions with simple oxide surface sites. In our study, the role of humic acids as a complexing ligand in the uptake of Cd^{2+} by hydrous iron oxide still remains largely inconclusive by the data in fresh water (Tables 21 and 22, and Figure 21). Further experiments are planned to study the adsorption of Cd^{2+} in seawater in the presence and absence of humic acids. Since in seawater, the suspended particles of hydrous iron oxide are better coated with humic acids, and so the effect of adsorbed humic acids on the uptake of Cd^{2+} may be better illustrated.

The adsorption data of humic acids and Cd^{2+} ion at pH equal 8.0 indicate that there is appreciable adsorption in the vicinity of PZC[8]. This behavior can be attributed only to the specific adsorption of humic acid and/or Cd^{2+} on hydrous iron oxide.

Since cadmium is a highly toxic pollutant, and often a component of industrial waste, it is useful to know whether this transition metal complex with humic acids is adsorbed. On the other hand, dissolved humic acids in solution may compete with the oxide surface for coordination of Cd^{2+} ions; Cd^{2+} adsorption may be decreased by complexing with the humic acids remaining in solution. This clearly points out the need for more research in order to solve problems of great significance.

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TABLES

TABLE 1: CONCENTRATION CHANGES OF FREE AND ADSORBED HUMIC ACIDS WITH TIME

(a): Freshly Prepared Hydrous Iron Oxide. Adsorption Experiment at 35°C.

	1	2	3	4	5	6	7	8
Initial Concentration of HA mg/ℓ	8.67	8.67	8.67	8.67	8.67	8.67	8.67	8.67
Time Elapsed (Hour)	0.5	2.0	5.0	8.3	18.5	24	31	42.5
Free [HA] in Solution mg/ℓ	6.22	4.60	2.77	1.22	1.02	0.93	0.87	0.93
[HA] Adsorbed on Iron Oxide mg/g	50.1	83.2	120.6	152.2	156.2	158.2	159.4	158.?

N.B. The concentration of suspension was 49.36 mg/ℓ

(b): Hydrous Iron Oxide in (a) Aged for Six Weeks.
Adsorption Experiment at 35°C.

	1	2	3	4	5	6	7
Initial Concentration of HA mg/	8.67	8.67	8.67	8.67	8.67	8.67	8.67
Time Elapsed (Hour)	0.5	2.0	6.5	18.7	24.1	30.0	48.0
Free [HA] in Solution mg/ℓ	4.25	3.07	2.17	1.75	1.47	1.48	1.25
[HA] Adsorbed on Iron Oxide mg/g	90.3	114.4	132.8	141.4	147.1	146.9	151.6

N.B. The concentration of suspension was 49.36 mg/ℓ.

(c): Hydrous Iron Oxide of Seed I. Absorption Experiment at 35°C.

	1	2	3	4	5	6
Initial Concentration of HA mg/ℓ	8.67	8.67	8.67	8.67	8.67	8.67
Time Elapsed (Hour)	0.5	1.5	4.0	8.5	20.0	26.0
Free [HA] in Solution mg/ℓ	8.28	8.17	7.83	7.42	6.57	6.55
[HA] Adsorbed on Iron Oxide mg/g	8.25	10.8	17.8	26.7	44.6	44.8

N.B. The concentration of suspension was 49.36 mg/ℓ

(d): Freshly Prepared Hydrous Iron Oxide.
Adsorption Experiment at 25°C.

	1	2	3	4	5	6	7	8
Initial Concentration of HA mg/ℓ	13.16	13.16	13.16	13.16	13.16	13.16	13.16	13.16
Time Elapsed (Hour)	0.5	1.5	4.5	9.5	19.0	25.0	31.5	42.5
Free [HA] in Solution mg/ℓ	6.41	5.51	3.14	2.19	1.67	1.58	1.48	.1.49
[HA] Adsorbed on Iron Oxide mg/g	138.6	157.0	205.7	225.2	235.9	237.7	239.8	239.6

N.B. The concentration of all above suspensions were 49.36 mg/ℓ

TABLE 2:   Adsorption of Humic Acids on Hydrous Iron Oxide*
in Fresh Water at $25°C$ - Expt. No. F1.

Reaction Flask No.	1	2	3	4	5	6
Free Humic Acids at Equilibrium C_f mg/ℓ	1.47	2.37	3.25	4.81	6.47	8.39
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	150.0	176.6	203.4	216.2	226.8	231.8
Γ/C_f	102.1	74.5	62.6	45.0	35.1	27.6

*Freshly prepared.

TABLE 3:   Adsorption of Humic Acids on Hydrous Iron Oxide*
in Fresh Water at $25°C$ - Expt. No. F2.

Reaction Flask No.	1	2	3	4	5	6	7	8	9	10
Free Humic Acid at Equilibrium C_f mg/ℓ	1.01	1.67	1.77	2.90	4.17	4.20	5.88	6.07	.7.45	9.17
Humic Acids Adsorbed on Iron Oxide Γ mg/g	114.4	145.9	143.9	165.7	184.6	183.9	194.2	190.3	206.6	215.7
Γ/C_f	113.3	87.4	81.3	57.1	44.3	43.8	33.0	31.4	27.7	23.5

*Freshly prepared.

TABLE 4:   Adsorption of Humic Acids on Hydron Iron Oxide*
in Fresh Water at $25^{\circ}C$ - Expt. No. F3.

Reaction Flask No.	1	2	3	4	5	6	7	8	9	10
Free Humic Acids at Equilibrium C_f mg/l	1.30	1.35	2.23	3.22	3.35	5.28	5.38	6.75	6.82	8.3
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	108.5	107.5	134.5	159.2	156.5	161.8	159.7	176.3	174.9	187
Γ/C_f	83.5	79.6	60.3	49.4	46.7	30.6	29.7	26.1	25.6	22.

*Freshly prepared.

TABLE 5:   Adsorption of Humic Acids on Hydrous Iron Oxide*
in Fresh Water at $25^{\circ}C$ - Expt. No. F4.

Reaction Flask No.	1	2	3	4	5	6	7	8
Free Humic Acid at Equilibrium C_f mg/l	0.52	1.13	1.90	3.17	4.38	5.58	7.77	9.60
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	71.0	120.0	141.2	160.2	180.2	200.4	200.0	206.8
Γ/C_f	137.0	99.1	74.3	50.5	41.2	35.9	25.7	21.6

*Freshly prepared.

TABLE 6: Adsorption of Humic Acids on Hydrous Iron Oxide*
in Fresh Water at 25°C - Expt. No. F5.

Reaction Flask No.	1	2	3	4	5	6	7	8	9	10	11
Free Humic Acids at Equilibrium, C_f mg/ℓ	0.69	0.69	1.30	1.30	2.08	3.92	4.05	5.42	5.42	6.17	8.19
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	120.9	120.9	153.5	153.5	182.5	189.7	187.0	203.7	203.7	188.2	191.3
Γ/C_f	175.3	175.3	118.1	118.8	87.7	48.4	46.2	37.6	37.6	30.5	23.4

*Freshly prepared.

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TABLE7:   Adsorption of Humic Acids on Hydrous Iron Oxide[*]
in Sea Water at $35^{\circ}C$ - Expt. No. SW1.

Reaction Flask No.	1	2	3	4	5	6
Free Humic Acids at Equilibrium, C_f mg/l	0.12	0.32	0.73	1.69	3.56	5.95
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	58.1	94.4	126.0	146.5	168.1	178.9
Γ/C_f	484.5	295.0	172.6	86.7	47.2	30.1

[*]Freshly prepared.

TABLE 8:   Adsorption of Humic Acids on Hydrous Iron Oxide[*]
in SeaWater at $35^{\circ}C$ - Expt. No. SW2.

Reaction Flask No.	1	2	3	4	5	6
Free Humic Acid at Equilibrium .C_f mg/l	0.34	0.50	0.91	1.94	3.25	4.94
Humic Acid, Adsorbed on Iron Oxide, Γ mg/g	73.7	70.5	102.3	121.6	134.7	140.2
Γ/C_f	216.9	141.0	117.4	62.7	41.5	28.4

[*]Freshly prepared.

TABLE 9:   Adsorption of Humic Acids on Hydrous Iron Oxide*
in Seawater at $35^\circ C$ - Expt. No. SW3.

Reaction Flask No.	1	2	3	4	5
Free Humic Acids at Equilibrium C_f mg/ℓ	0.83	1.76	3.33	5.06	6.94
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	63.8	85.1	93.4	98.1	99.7
Γ/C_f	76.9	48.3	28.0	19.4	14.4

*Freshly prepared.

TABLE 10:   Adsorption of Humic Acids on Hydrous Iron Oxide*
in Seawater at $35^\circ C$ - Expt. No. SW4.

Reaction Flask No.	1	2	3	4	5
Free Humic Acid at Equilibrium C_f mg/ℓ	0.14	0.33	2.24	4.84	6.64
Humic Acid Adsorbed on Iron Oxide Γ mg/g	37.7	73.9	115.5	142.2	145.2
Γ/C_f	269.3	224.1	51.6	29.4	21.9

TABLE 11: Adsorption of Humic Acids on Hydrous Iron Oxide*
in Seawater at 35°C - Expt. No. SW5.

Reaction Flask No.	1	2	3	4
Free Humic Acid at Equilibrium C_f mg/ℓ	0.50	1.35	2.89	4.28
Humic Acids Adsorbed on Iron Oxide Γ mg/g	70.5	93.4	102.3	113.9
Γ/C_f	140.0	69.2	35.4	26.6

*Freshly prepared.

TABLE 12: Adsorption of Humic Acids on Hydrous Iron Oxide
Seed I in Seawater at 35°C. - Expt. No. SDI.

Reaction Flask No.	1	2	3	4
Free Humic Acid at Equilibrium C_f mg/ℓ	1.07	1.65	3.33	5.32
Humic Acids Adsorbed on Iron Oxide Γ mg/g	34.0	41.3	46.6	46.4
Γ/C_f	31.8	25.0	14.0	8.7

TABLE 13: Adsorption of Humic Acids on Hydrous Iron Oxide Seed III in Seawater at 25°C - Expt. No. SDIII-1.

Reaction Flask No.	1	2	3	4	5	6	7
Free Humic Acid at Equilibrium C_f mg/ℓ	0.28	0.40	0.79	0.87	1.28	1.54	2.45
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	58.1	98.1	132.0	172.5	205.7	241.9	264.1
Γ/C_f	207.3	245.3	167.0	198.2	160.7	157.1	107.8

TABLE 14: Adsorption of Humic Acids on Hydrous Iron Oxide Seed III in Seawater at 25°C - Expt. No. SDIII-2.

Reaction Flask No.	1	2	3	4	5	6	7
Free Humic Acid at Equilibrium C_f mg/ℓ	0.30	0.47	0.68	0.92	1.39	1.85	2.34
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	57.6	96.6	134.3	171.4	203.3	235.2	266.5
Γ/C_f	182.1	205.6	197.5	186.3	146.3	127.2	113.9

TABLE 15:   Adsorption of Humic Acids on Hydrous Iron Oxide
            Seed V in Seawater at 35°C - Expt. N o. SDV-1.

Reaction Flask No.	1	2	3	4	5	6
Free Humic Acid at Equilibrium C_f mg/ℓ	0.27	0.38	0.50	0.70	0.88	1.02
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	88.3	123.2	157.9	190.9	224.1	258.1
Γ/C_f	327.2	324.3	315.8	272.8	254.7	253.0

Aged 24 hours.

TABLE 16:   Adsorption of Humic Acids on Hydrous Iron Oxide
            Seed V* in Fresh Water at 35°C - Expt. No. SDV-2.

Reaction Flask No.	1	2	3	4	5	6	7	8
Free Humic Acid Equilibrium C_f mg/ℓ	0.46	0.83	1.25	1.77	2.13	2.63	3.65	4.54
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	47.5	77.8	107.3	134.1	164.1	191.3	208.8	228.4
Γ/C_f	103.2	93.8	85.8	75.8	77.1	72.7	57.2	50.3

*Aged 24 hours.

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TABLE 17: Adsorption of Humic Acids on Hydrous Iron Oxide Seed V* in Fresh Water at $35^{\circ}C$ - Expt. No. SDV-3.

Reaction Flask No.	1	2	3	4	5
Free Humic Acids at Equilibrium C_f mg/ℓ	0.69	1.29	1.21	2.30	3.44
Humic Acids Adsorbed on Iron Oxide, Γ mg/g	47.7	76.6	78.2	117.0	134.0
Γ/C_f	69.2	59.4	64 6	50.9	39.0

*Aged for 8 weeks.

TABLE 18:   Adsorption of Humic Acids on Hydrous Iron Oxide at 25°C and 35°C. Surface Concentations Γ, on Various Seeds With and Without Aging.

	a	b	c	d
Hydrous Iron Oxide	Freshly prepared	From a. Aged 6 wks.	Seed I. Aged 5 wks.	Freshly prepared.
Temperature of Bath	35°C	35°C	35°C	25°C
Co, Initial Concentration of HA mg/ℓ	8.67	8.67	8.67	13.16
Γ [HA] Absorbed on Iron Oxide at Equilibrium mg/g	158.4 mg/g	146.9	44.6	236.0

N.B.   All concentrations of suspensions = 49.36 mg/ℓ

TABLE 19:   Adsorption of Humic Acids on Hydrous Iron Oxide at 35°C. Surface Concentations Γ, on Various Seeds of Different Sizes.

	a	b
Hydrous Iron Oxide	Freshly prepared.	Freshly prepared
Temperature of Bath	35°C	35°C
Co, Initial Concentrations of HA mg/ℓ	8.67	8.67
Sizes* of Particles (length in µm)	4.2	4.7
Γ [HA] Adsorbed on Iron Oxide at Equilibrium mg/g	7.75 158.37 mg/g	6.72 137.32 mg/g

N.B.   All concentrations of suspensions = 49.36 mg/ℓ.

*PA-720 HIAC Particle Size Analyser was used.

TABLE 20:   Adsorption Parameters of Humic Acids on Hydrous Iron Oxide.

Expt. No.	Temp. °C	Suspension Conc mg/	Γ_m	K_l	Correlation Coefficient r	Avg. Size μm	Remarks
F1	25	48.8±0.3	266	0.88	.989	-	Fresh Water
F2	"	"	231	0.95	.986	-	"
F3	"	"	206	0.85	.967	-	"
F4	"	"	231	0.86	.977	-	"
F5	"	"	214	1.94	.967	-	"
SW1	35	48.8±0.3	177	3.88	.986	2.7	Sea Water
SW2	"	"	147	2.55	.929	6.2	"
SW3*	"	"	109	1.76	.991	4.9	"
SW4	"	"	149	2.61	.976	3.1	"
SW5	"	"	119	2.89	.981	-	"
SDI	35	55.0±0.4	53	1.87	.945	-	Sea Water
SDIII-1	25	46.3±0.3	435	0.64	.847	-	"
SDIII-2	"	"	435	0.64	.847	-	"
SDV-1	35	52.8±0.3	614	0.67	.950	5.5	Sea Water
SDV-2	"	"	418	0.28	.967	"	Fresh Water
SDV-3*	"	"	248	0.36	.963	"	"

K_l is adsorption equilibrium constant; Γ_m is monolayer adsorption, mg/g.
*Seeds were aged for more than 6 weeks.
N.B. (1) Initial concentration of humic acids in suspensions were less than
15 mg/ℓ to avoid coagulation when seawater used as medium.
(2) PA-720 HIAC Particle Size Analyser was used to estimate the average
size of particles.

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TABLE 21: Adsorption of Cadmium on Hydrous Iron Oxide
Seed V in Fresh Water at $35^{\circ}C$ - Expt. No. Cd1

	1	2	3	4	5	6
Free Cadmium at Equilibrium, C_f, µg/ℓ	0	0	.01	.04	.03	.07
Cadmium Adsorbed on Iron Oxide, Γ µg/g	0	62.0	123.4	204.6	285.9	365.4

TABLE 22: Adsorption of Cadmium on Hydrous Iron Oxide
Seed V in the Presence of Humic Acid in
Fresh Water at $35^{\circ}C$ - Expt. No. Cd2

	1	2	3	4	5	6
Free Cadmium at Equilibrium, C_f, µg/	0	.06	.14	.22	.37	.40
Cadmium Adsorbed on Iron Oxide, Γ µg/g	0	60.8	120.7	200.8	278.8	358.5

TABLE 23: Adsorption of Cadmium on Hydrous Iron Oxide
Seed V in Seawater at $35^{\circ}C$ - Expt. No. Cd3

	1	2	3	4	5	6
Free Cadmium at Equilibrium C_f, $\mu g/g$	0	2.15	3.93	6.22	9.33	11.64
Cadmium Adsorbed on Iron Oxide, Γ $\mu g/g$	0	17.4	42.1	76.3	92.9	125.3

FIGURES
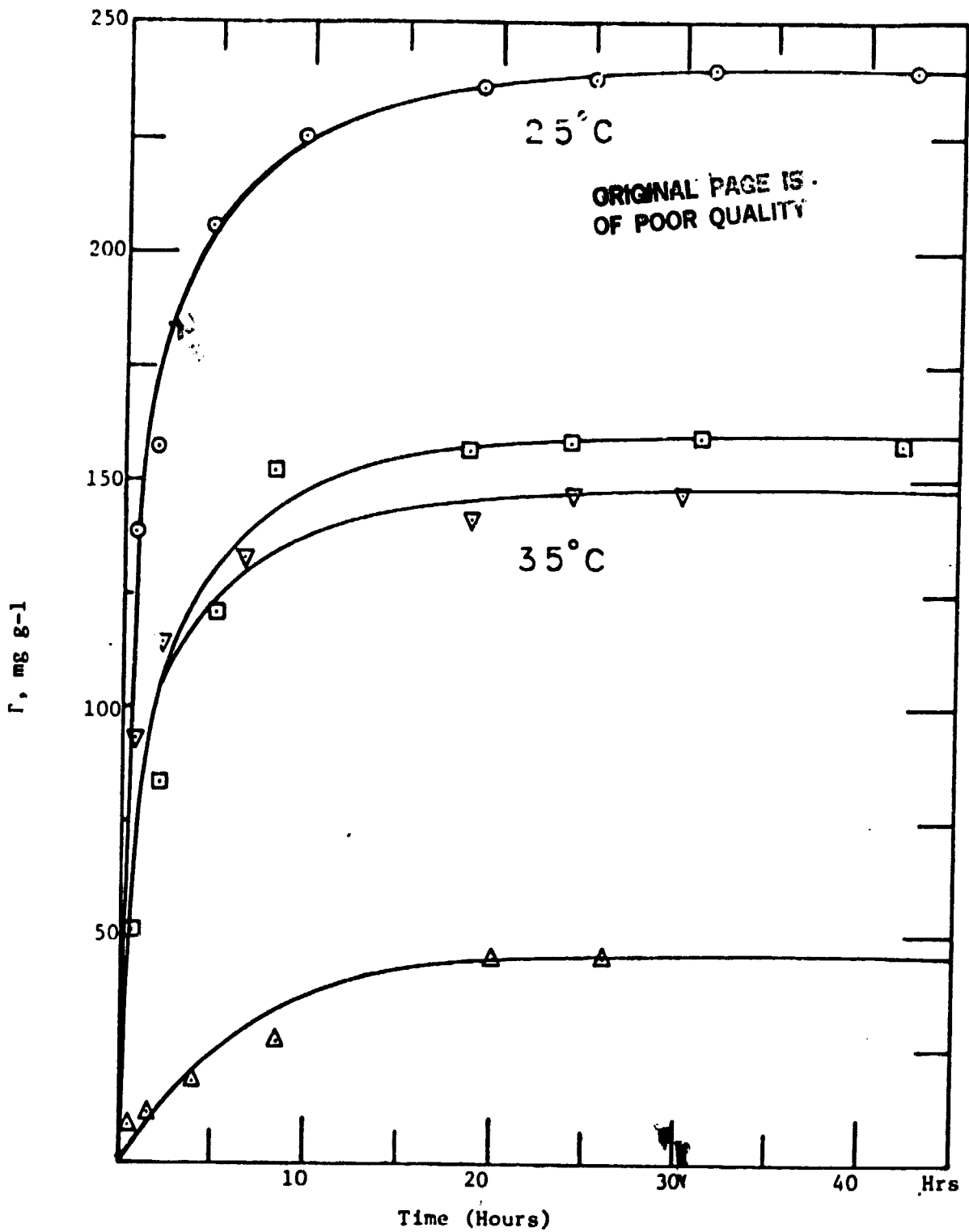
Fig. 1: Plot of Surface Concentration, Γ Against Time.
(o) Expt. A; (△) Expt. SD-1; (▭) Expt. B1; (▽) Expt. B2
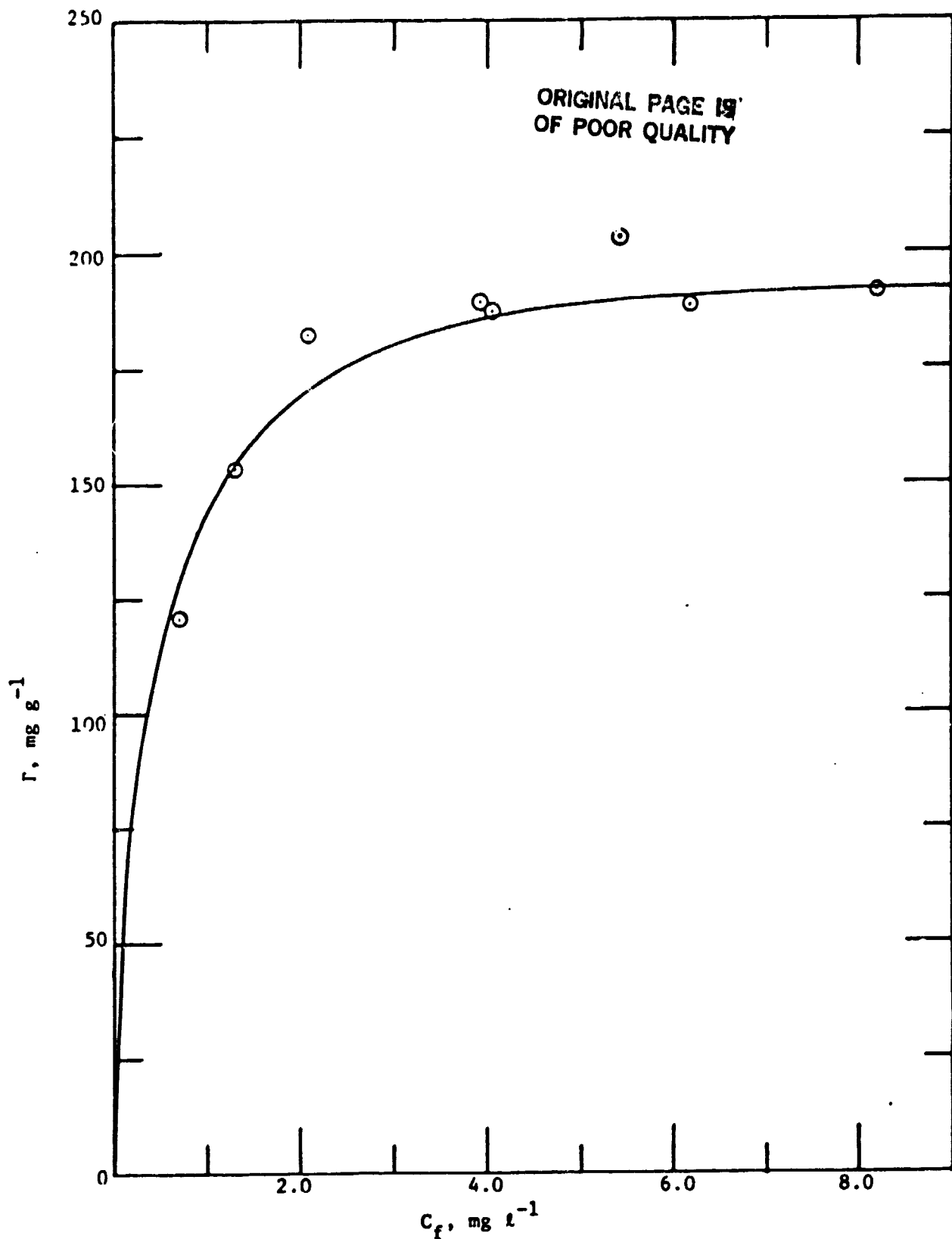
Fig. 2: Adsorption Isotherm in Fresh Water at $25^{\circ}C$. Plot of Surface
Concentration, Γ Against Free Humic Acids, C_f at Equilibrium.
Expt. F5.

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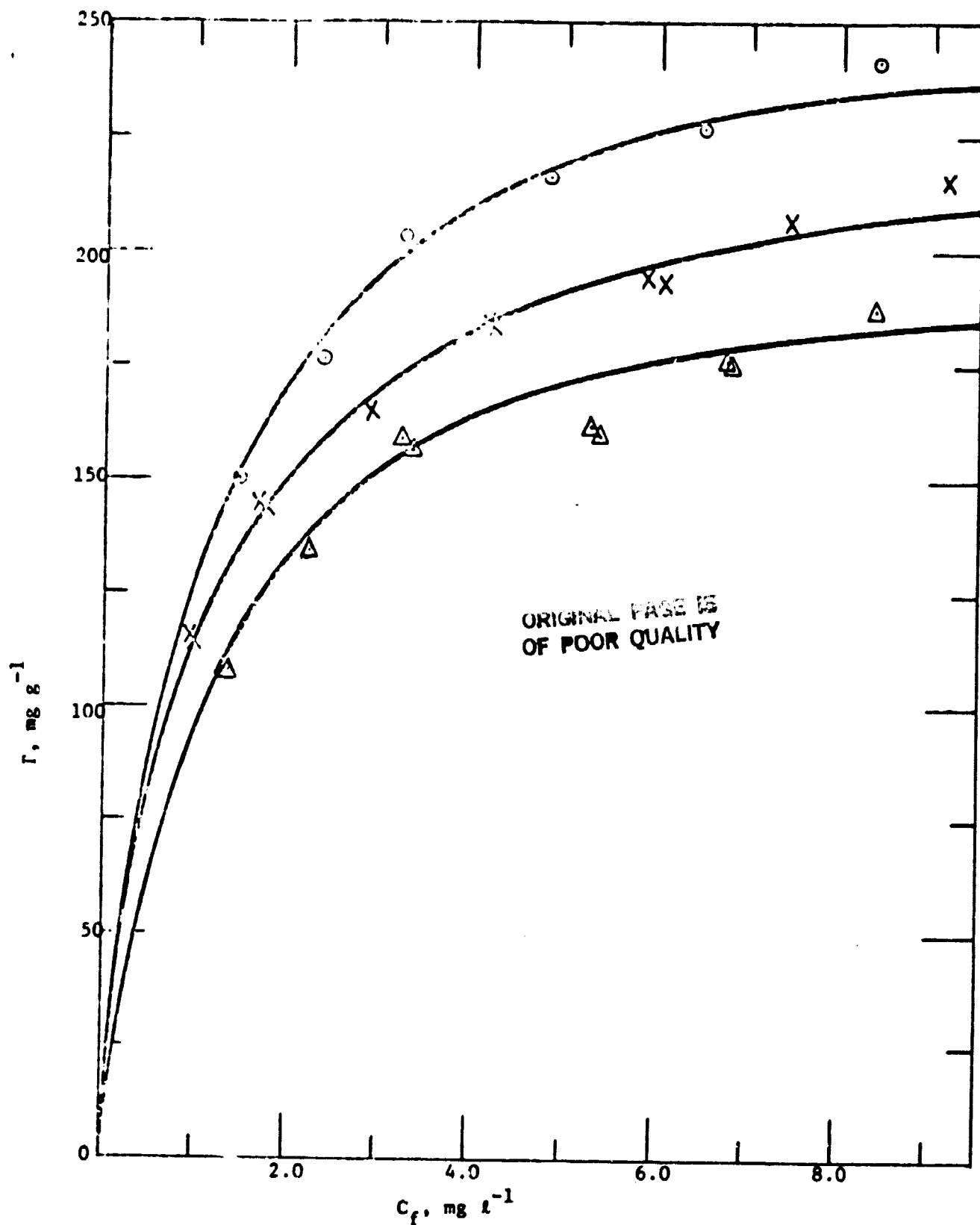
Fig. 3: Adsorption Isotherms in Fresh Water at 25°C. Plot of Surface
Concentration, Γ Against Free Humic Acids, C_f at Equilibrium.
($\circ$) Expt. F1; ($\times$) Expt. F2; ($\triangle$) Expt. F3.
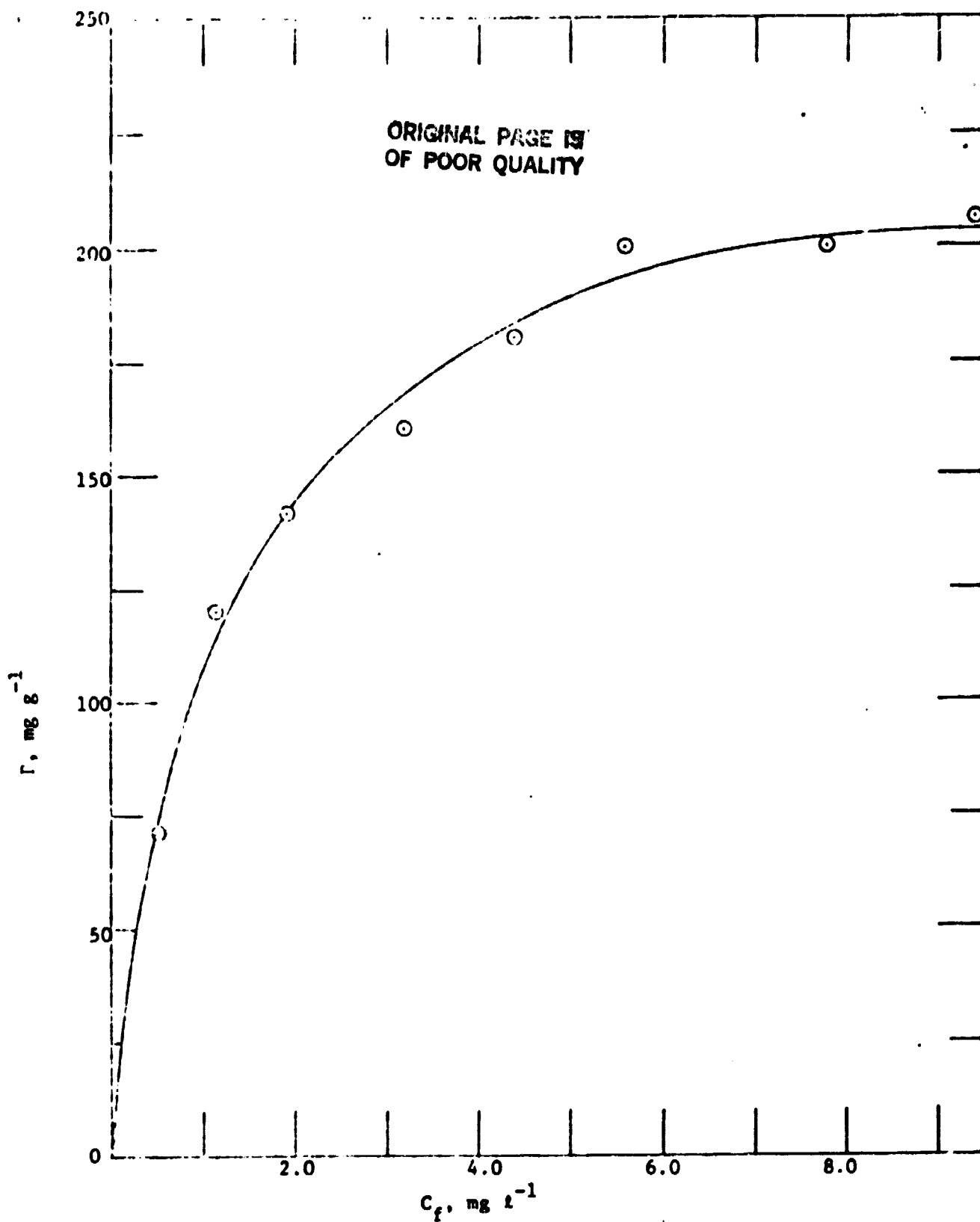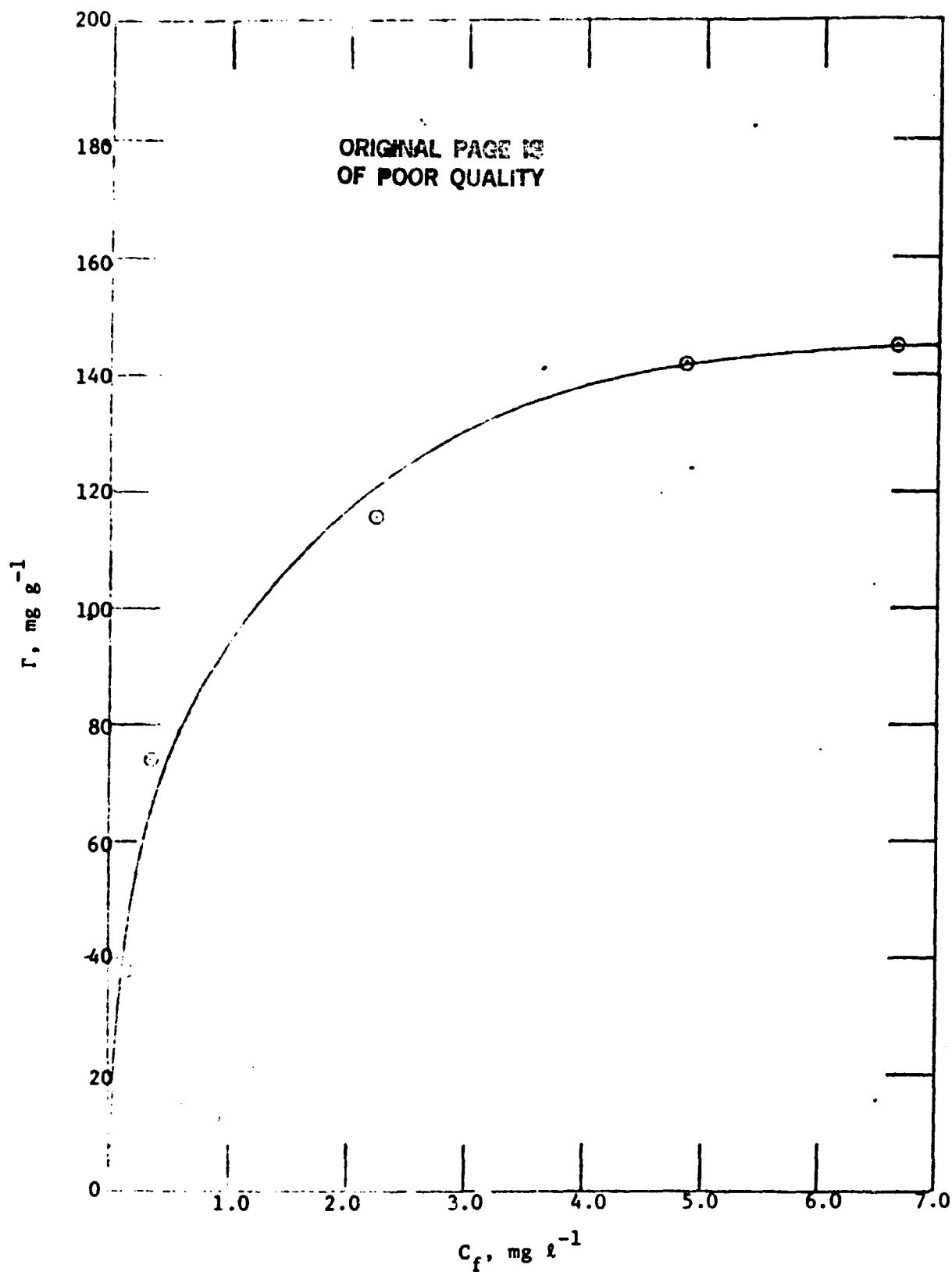
Fig. 4: Adsorption Isotherm in Fresh Water at 25°C. Plot of Surface
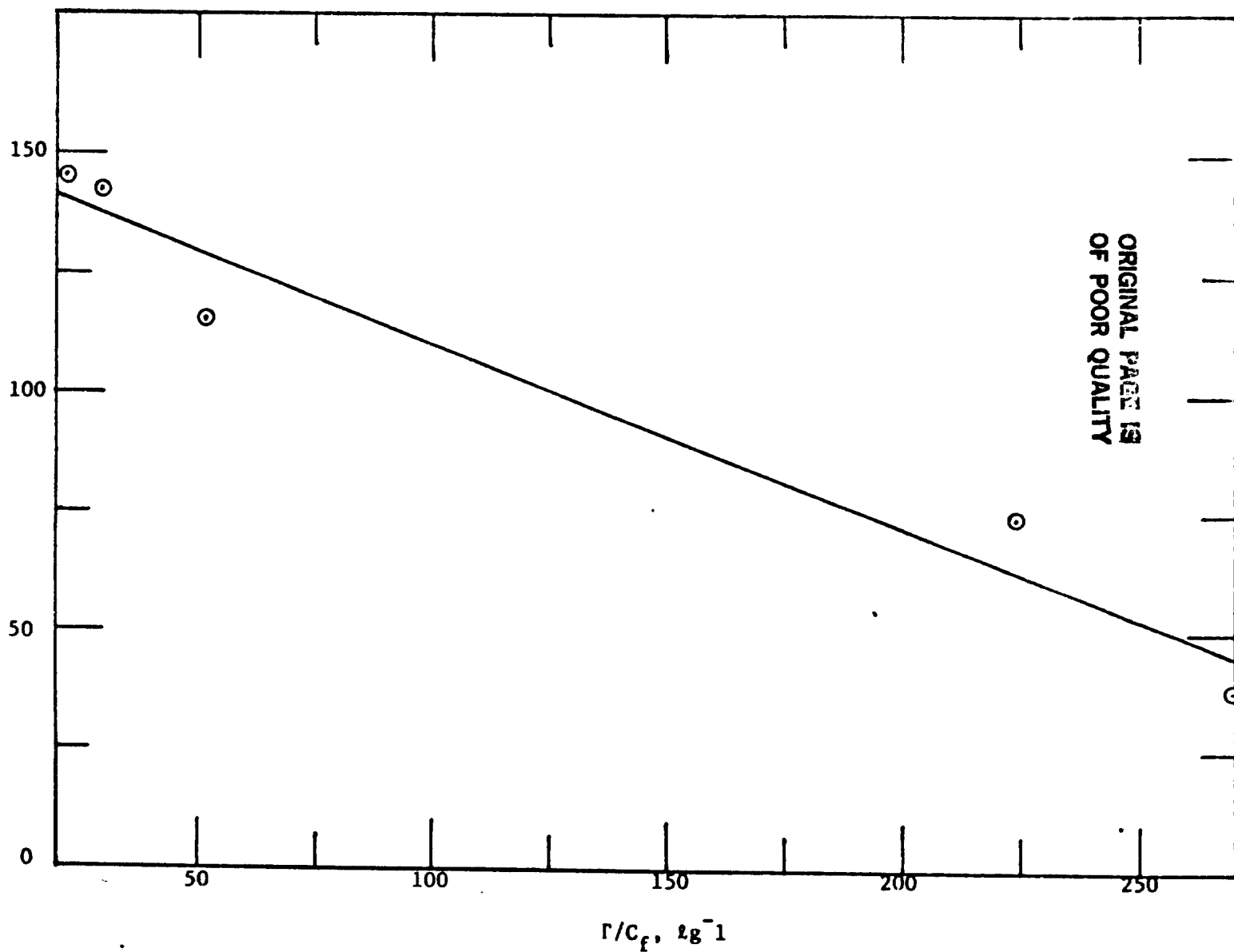Concentration, Γ Against Free Humic Acids, C_f at Equilibrium.
Expt. F4
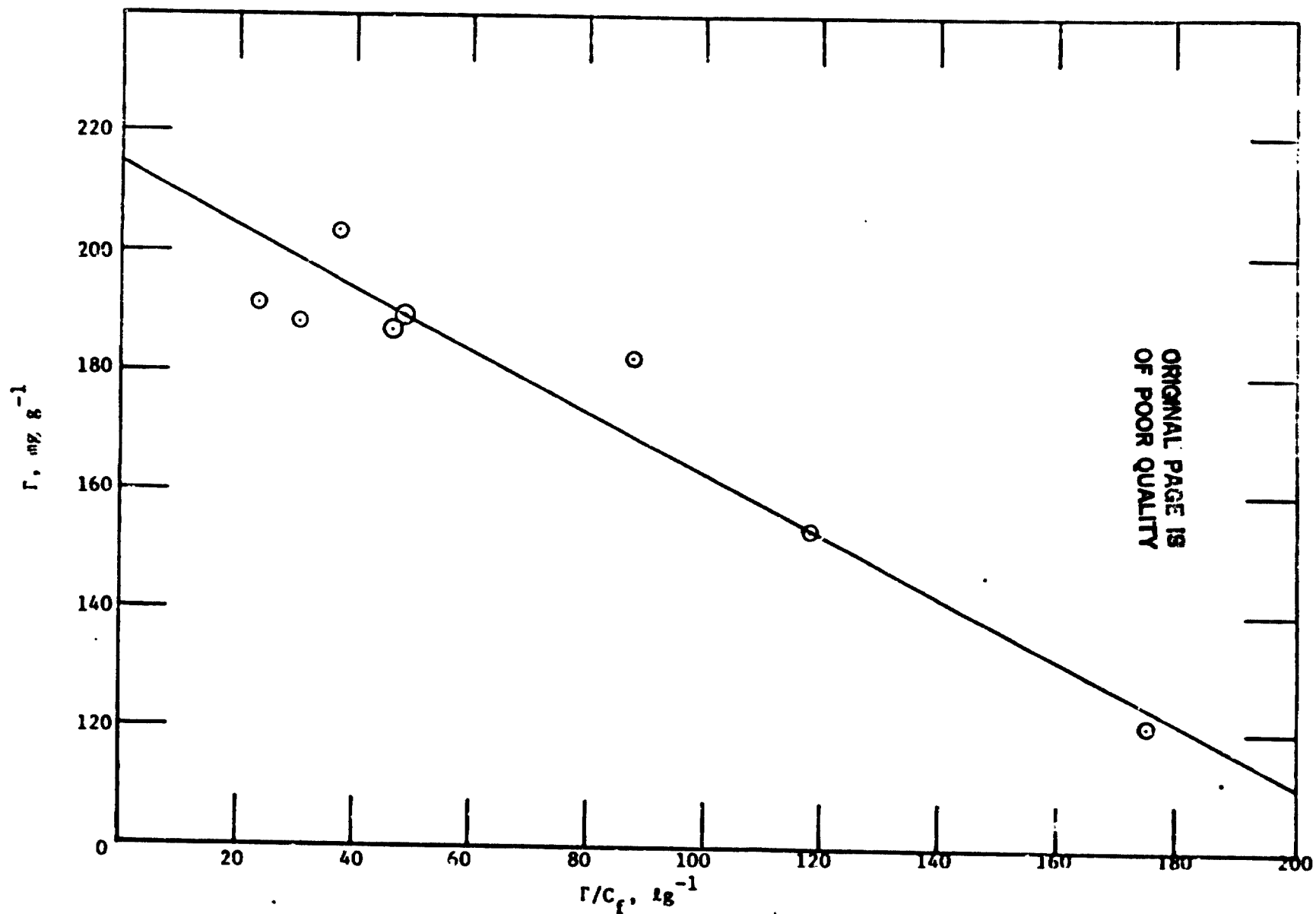
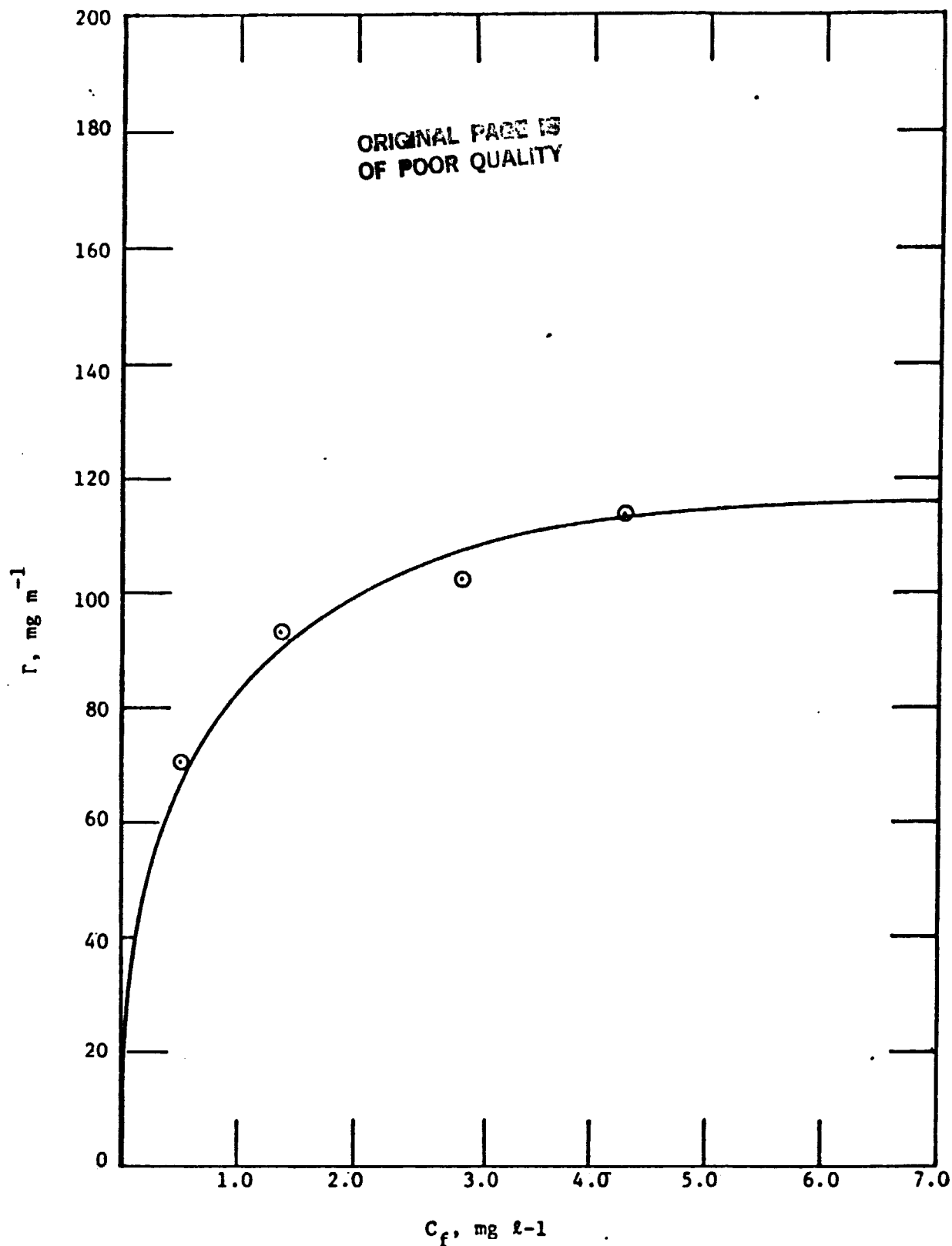Fig. 5: Langmiur Isotherm. Plot of Surface Concentration, Γ Against Γ/C_f.
       Expt. F5
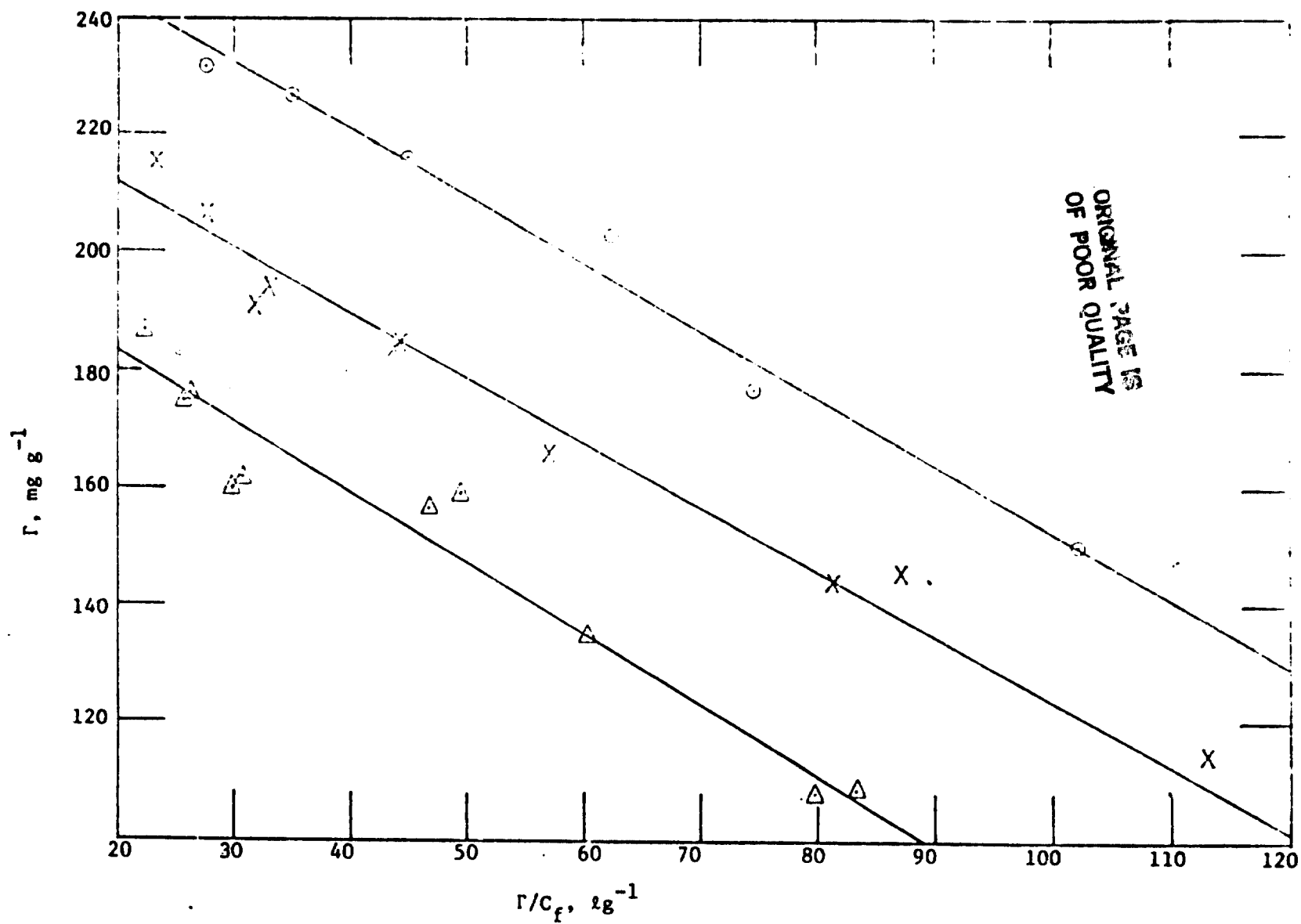
Fig. 6: Langmuir Isotherms. Plot of Surface Concentration, Γ Against Γ/C_f.
(o) Expt. F1; (X) Expt. F2; ($\triangle$) Expt. F3
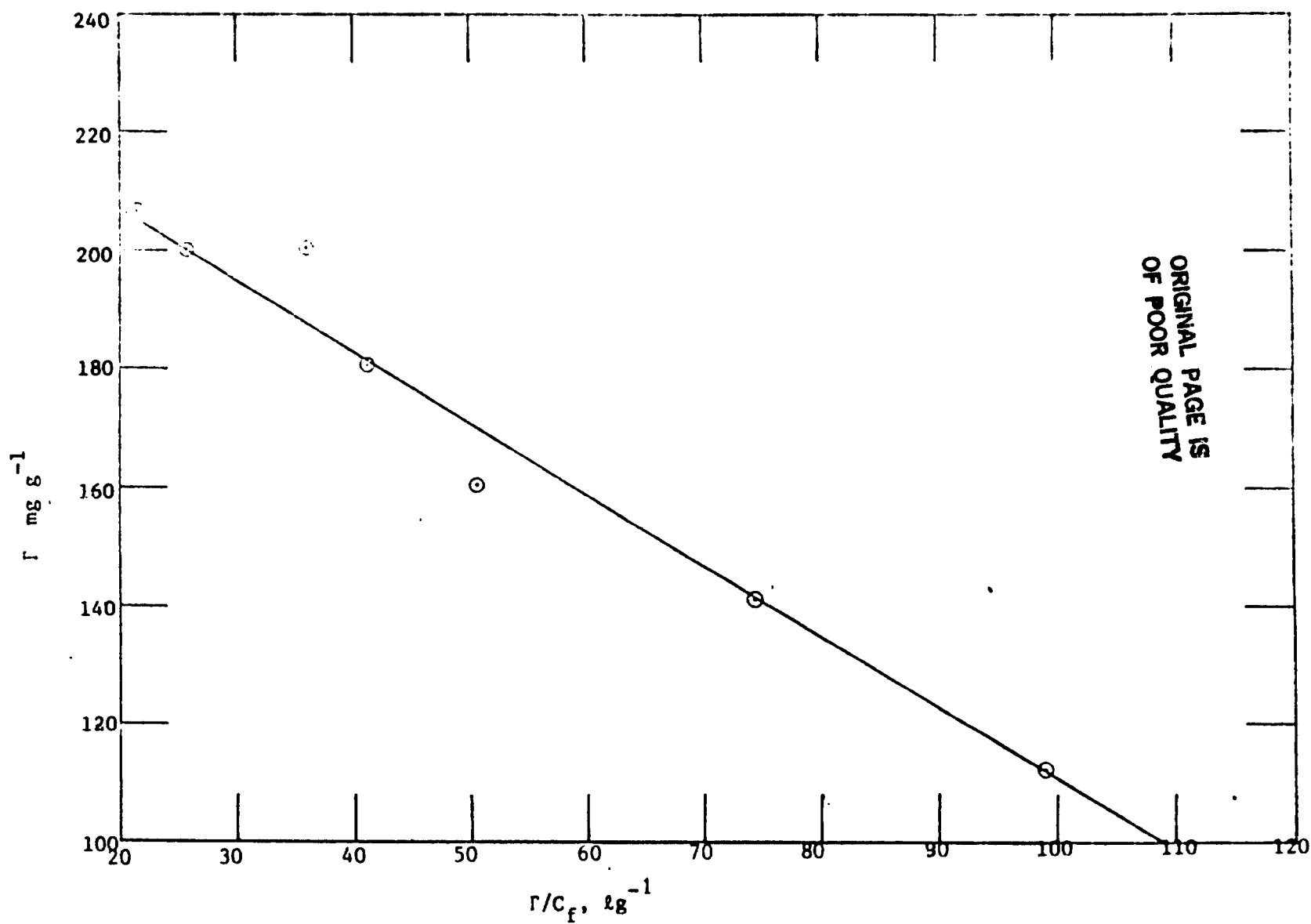
Fig. 7: Langmuir Isotherm. Plot of Surface Concentration, Γ Against Γ/C_f.
Expt. F4

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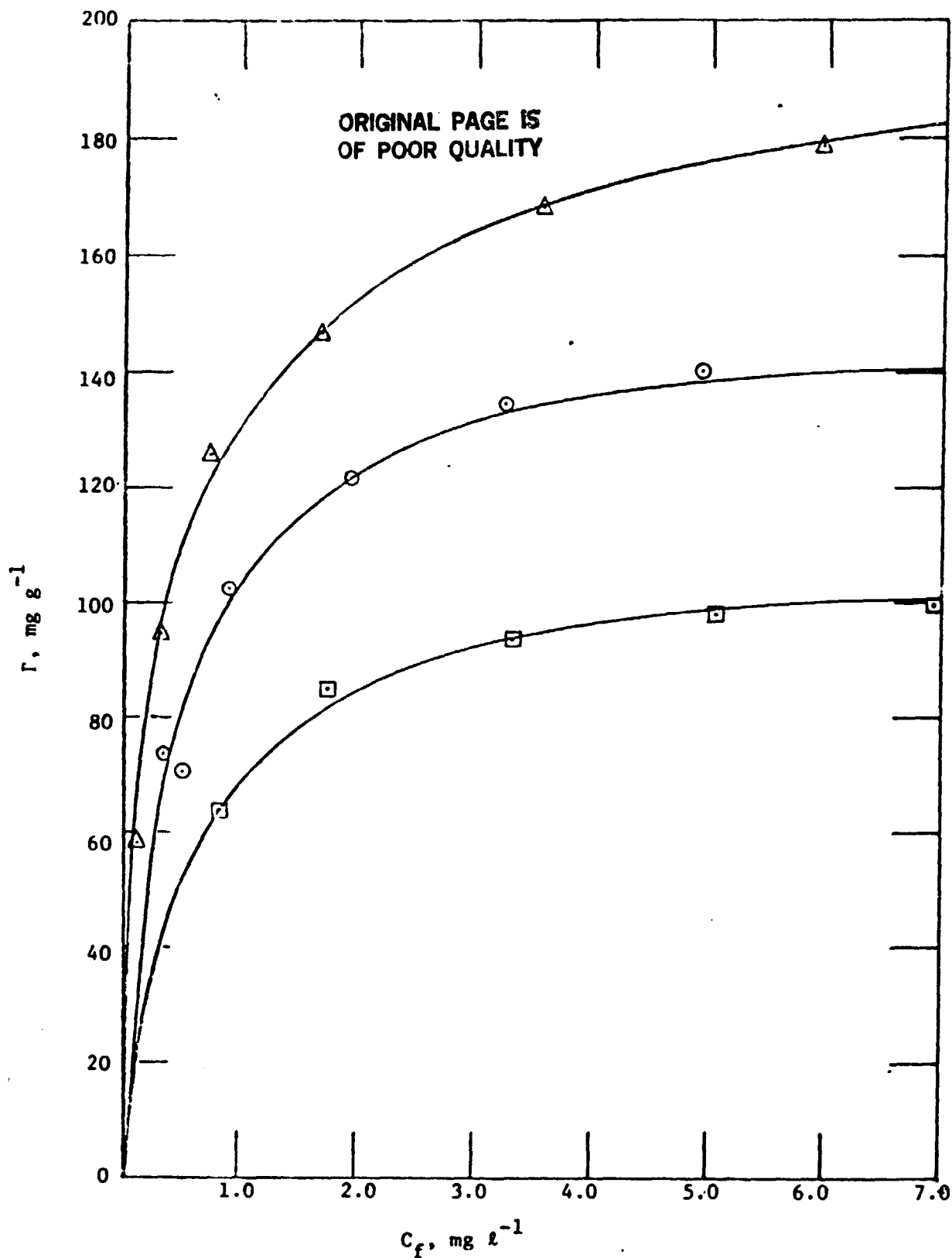
Fig. 8: Adsorption Isotherms in Seawater at 35°C. Plot of Surface
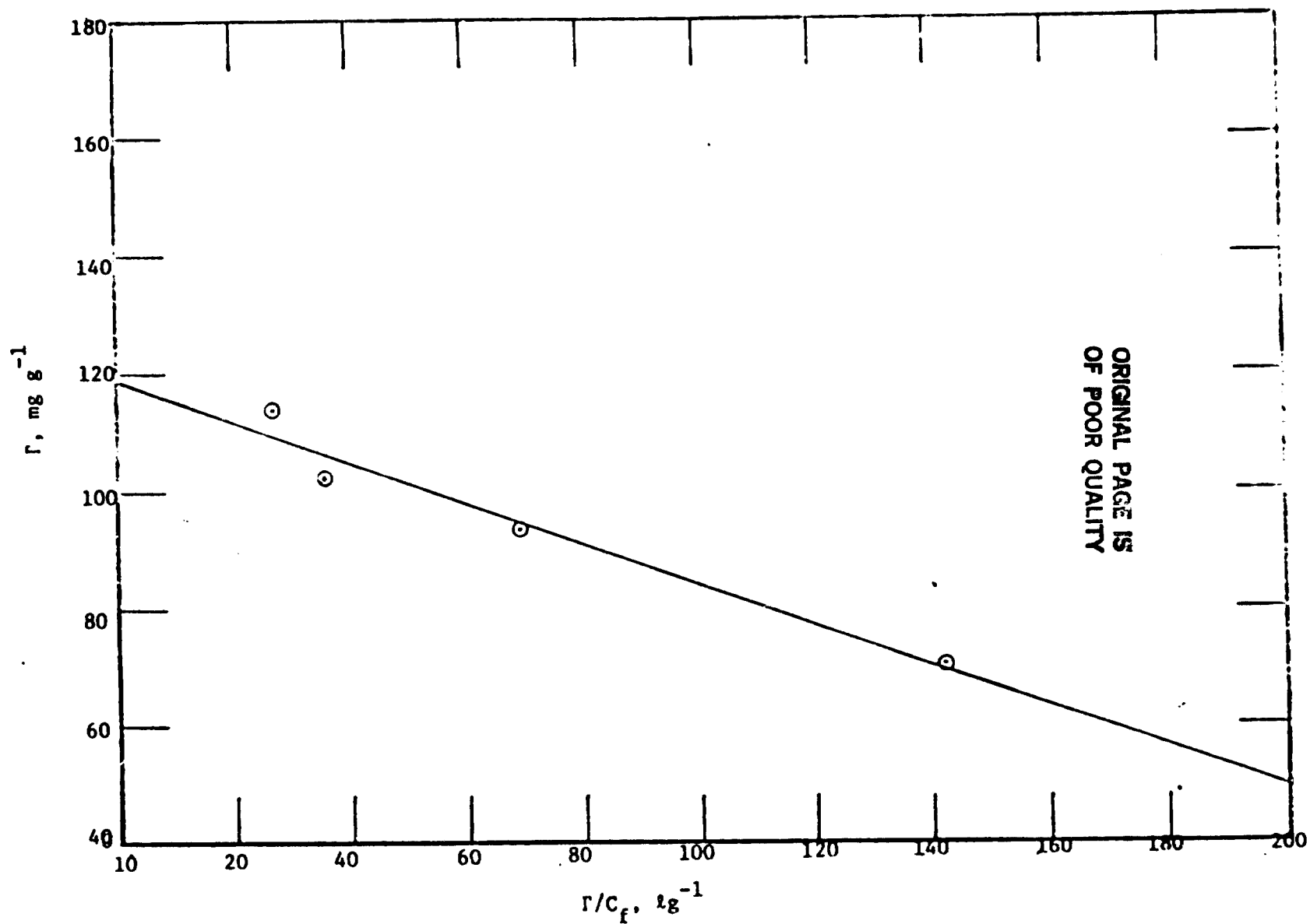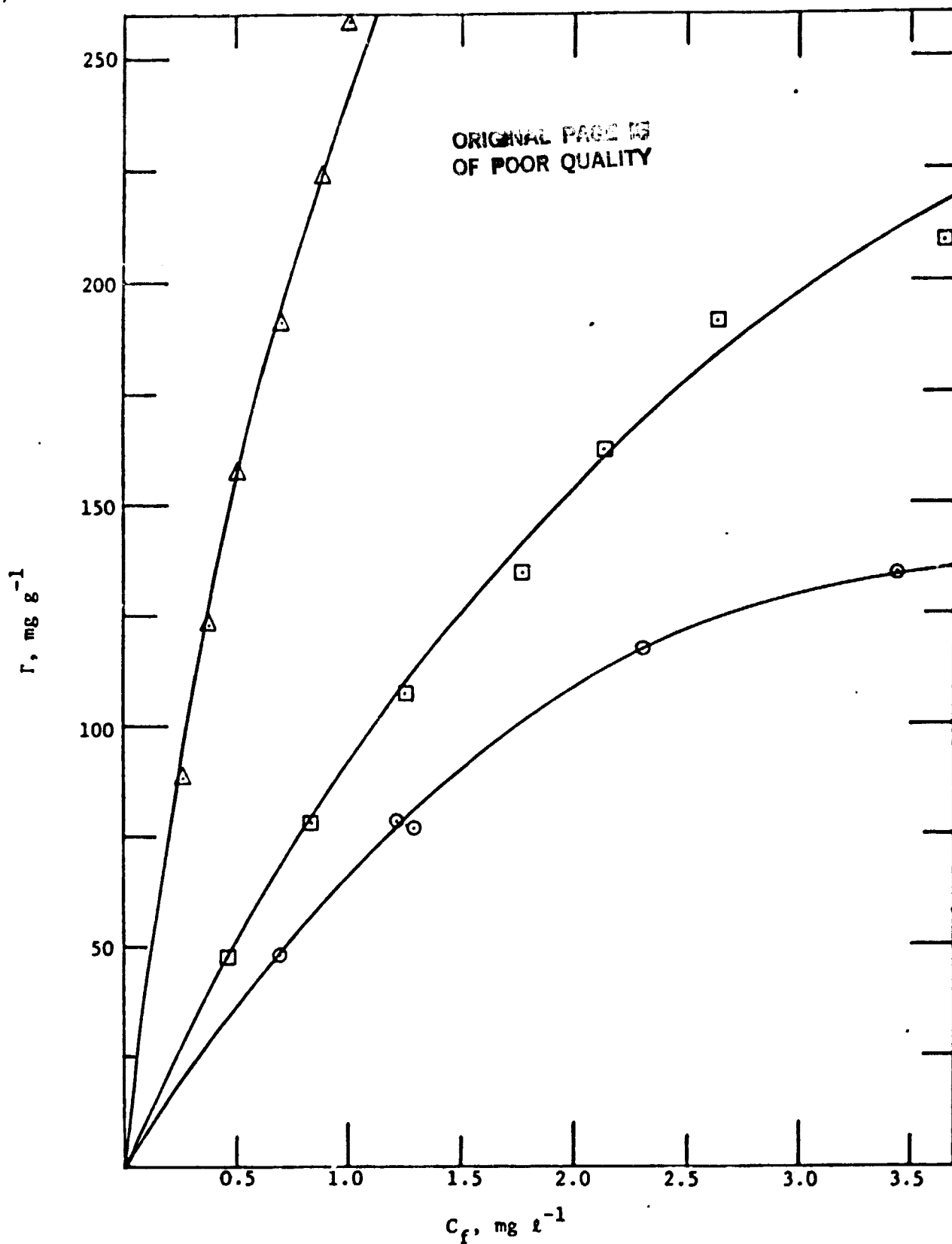Concentration, Γ Against Free Humic Acids, C_f at Equilibrium.
($\triangle$) Expt. SW1; ($\odot$) Expt. SW2; ($\square$) Expt. SW3
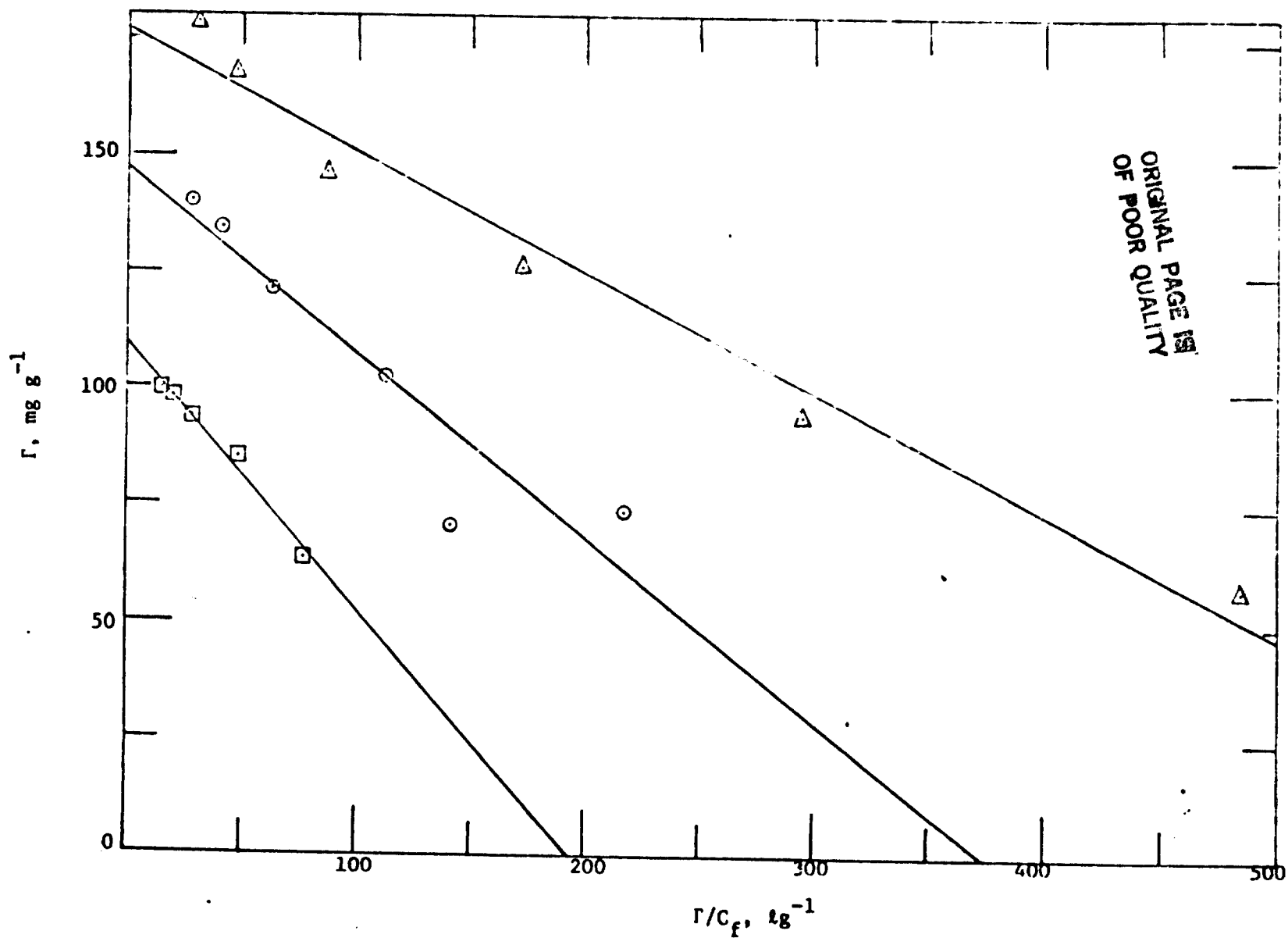
Fig. 9:   Langmuir Isotherms. Plot of Surface Concentration, Γ Against Γ/C_f.
(△) Expt. SW1; (o) Expt. SW2; (▱) Expt. SW3

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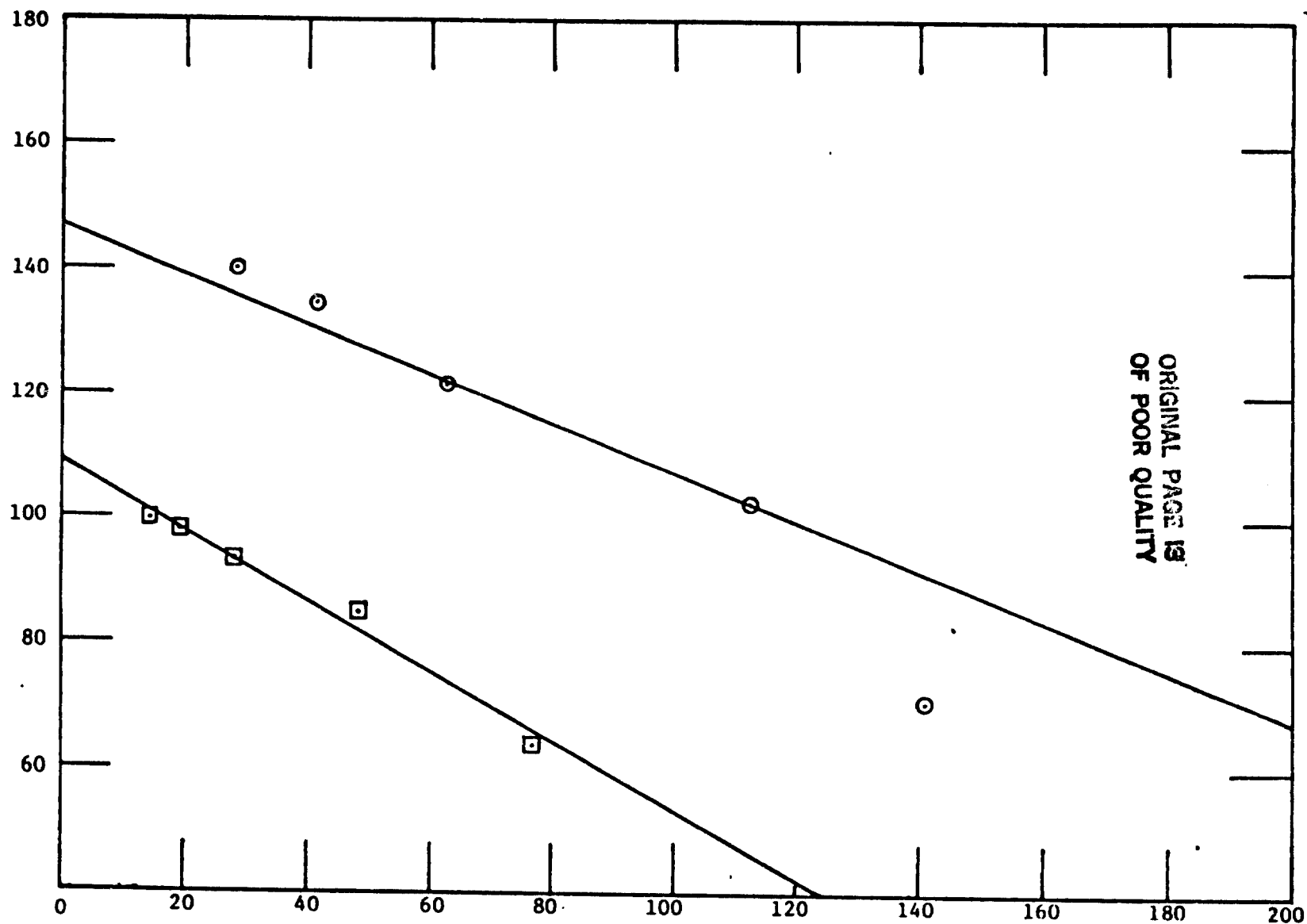
Fig. 10: Langmuir isotherms. Plot of surface concentration Γ against Γ/C_f.
(⊙) Expt. SW2; (⊡) Expt. SW3

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Fig. 11: Adsorption Isotherms in Seawater at $35^{\circ}C$. Plot of Surface
Concentration, Γ Against Free Humic Acids, C_f at Equilibrium.
Expt. SW4

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Fig. 12: Langmuir Isotherm. Plot of Surface Concentration, Γ Against Γ/C_f.
Expt. SW4

Fig. 13: Adsorption Isotherm in Seawater at 25°C. Plot of Surface
Concentration, Γ Against Free Humic Acids, C_f at Equilibrium.
Expt. SW5

Fig. 14:   Langmuir Isotherm.   Plot of Surface Concentration, Γ Against Γ/C_f.
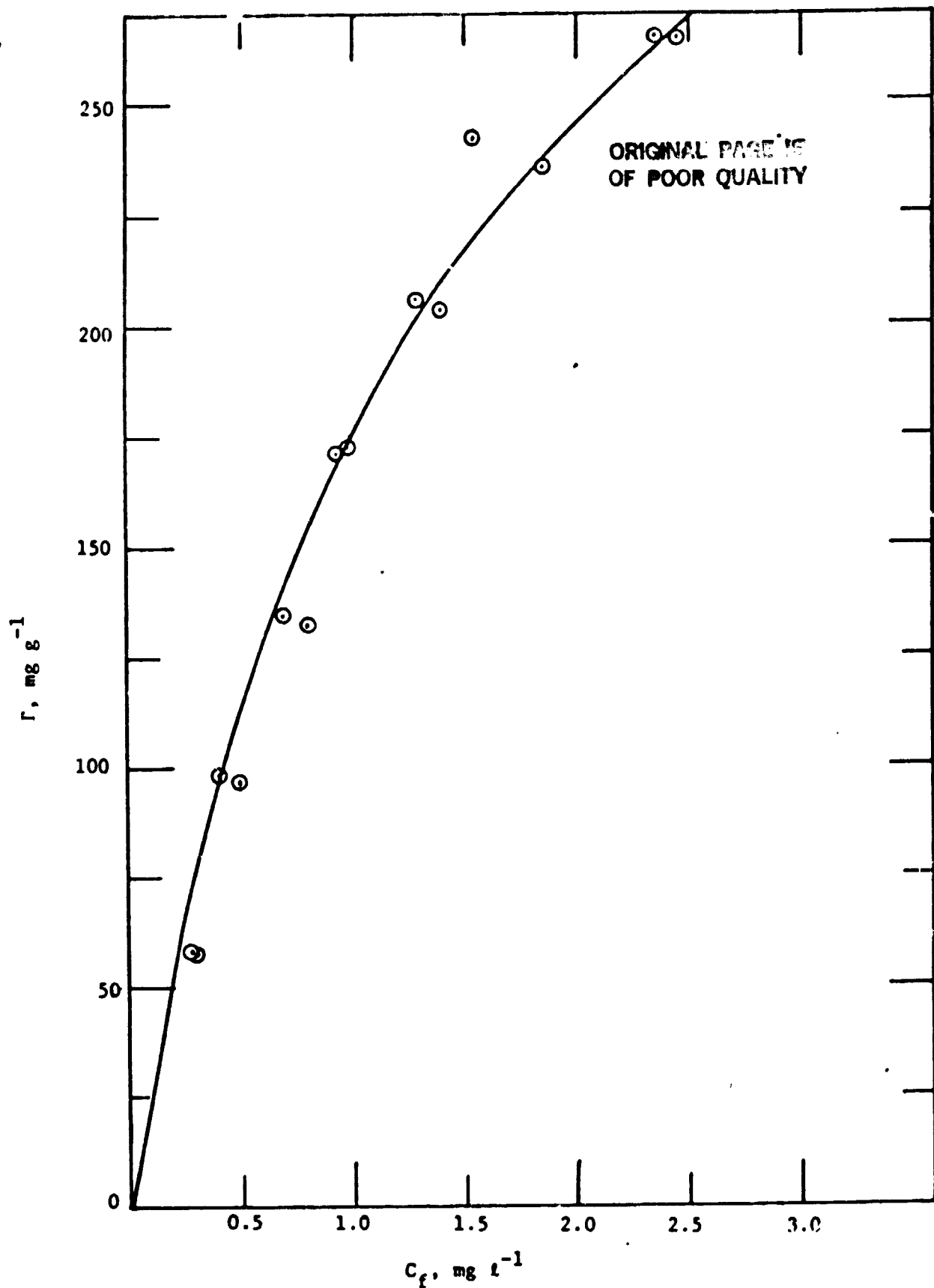Expt. SW5

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Fig. 15: Adsorption Isotherms at $35^{\circ}C$ for Hydrous Iron Oxide Seed V.
Plot of Surface Concentration, Γ Against Free Humic Acids,
C_f at Equilibrium.
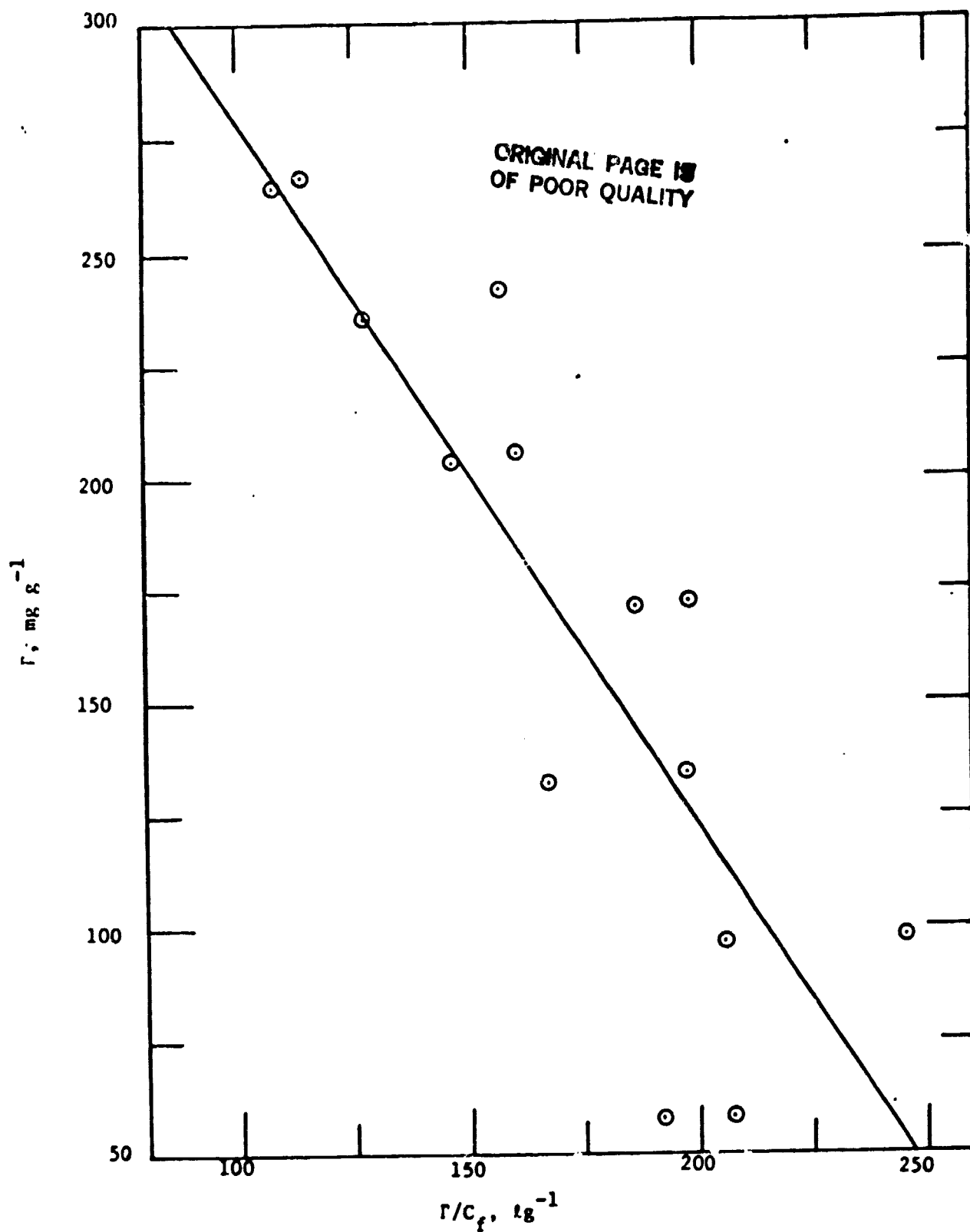($\triangle$) Expt. SDV-1; ($\square$) Expt. SDV-2; (o) Expt. SDV-3

Fig. 16: Langmuir Isotherms for Seed V. Plot of Surface Concentration, Γ Against Γ/C_f.
(△) Expt. SDV-1; (◻) Expt. SDV-2; (○) Expt. SDV-3

Fig. 17:   Adsorption Isotherms at $25^{\circ}C$ for Hydrous Iron Oxide Seed III.
Plot of Surface Concentration, Γ Against Free Humic Acids,
C_f at Equilibrium.   Expt. SD III

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Fig. 18: Langmuir Isotherm for Seed III. Plot of Surface
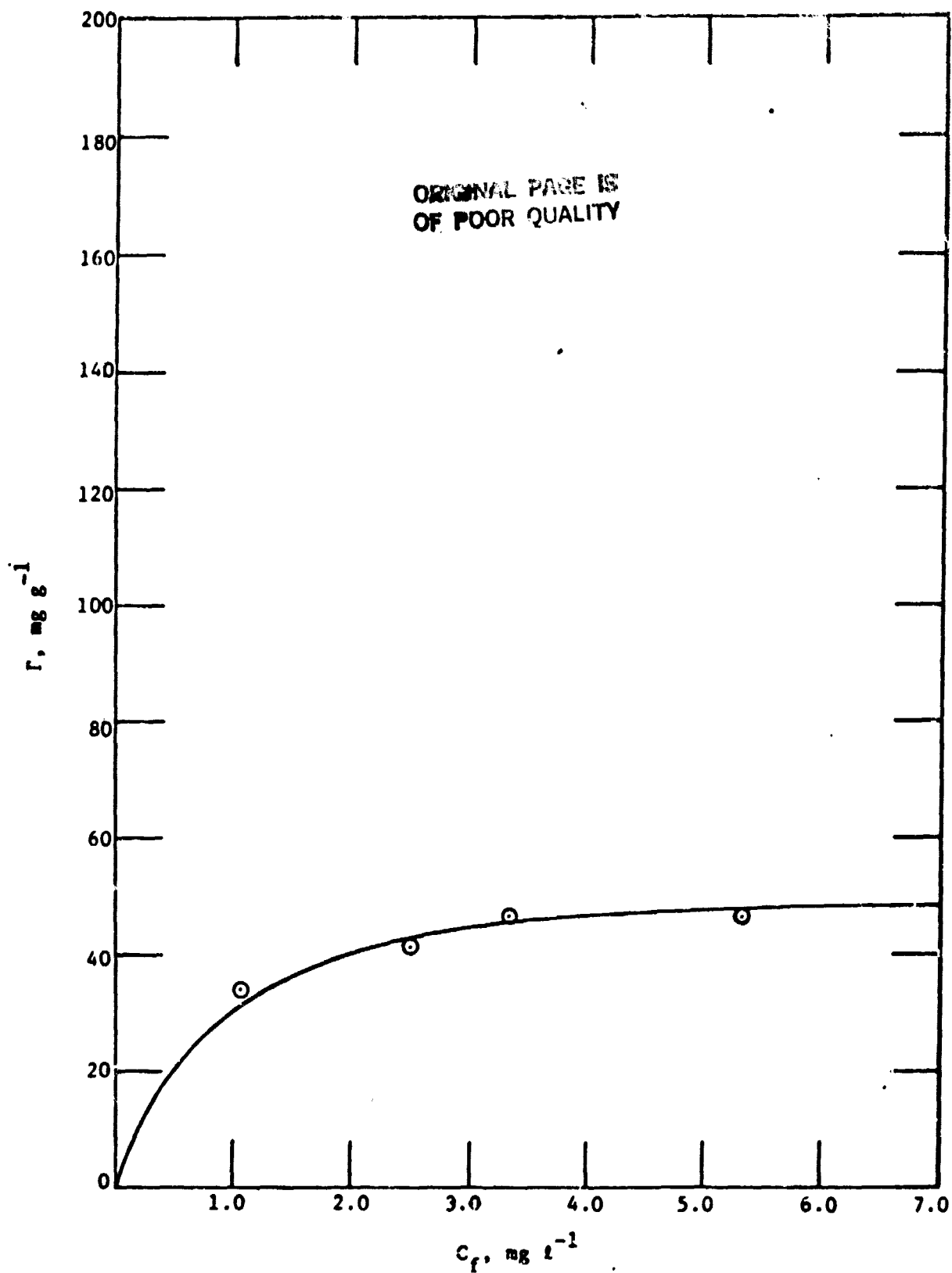Concentration, Γ Against Γ/C_f. Expt. SD III

Fig. 19: Adsorption Isotherm at $35^\circ C$ for Hydrous Iron Oxide Seed I.
Plot of Surface Concentration, Γ Against Free Humic Acids,
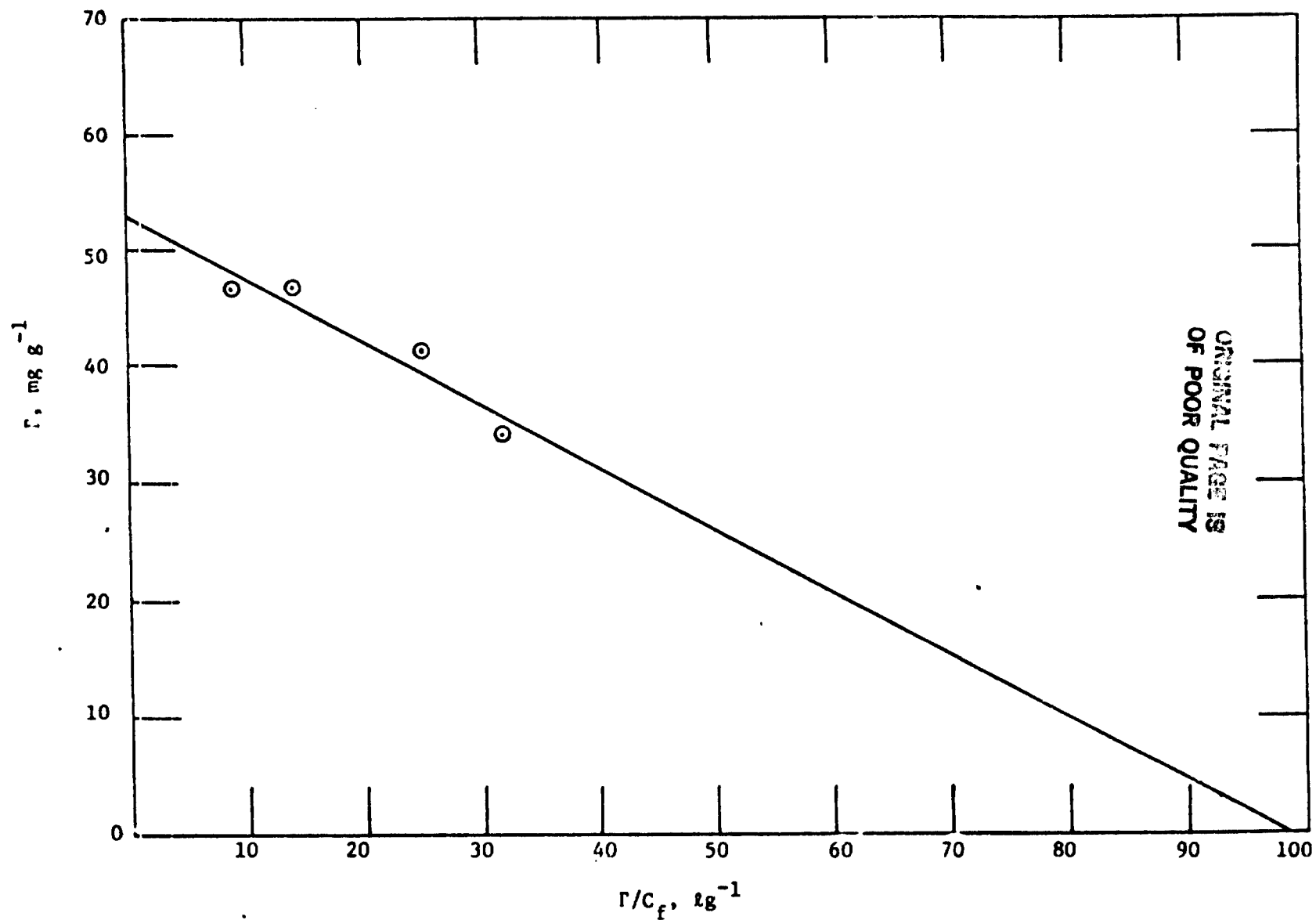C_f at Equilibrium. Expt. SDI-2

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Fig. 20:   Langmuir Isotherm for Seed I.   Plot of Surface Concentration, Γ Against Γ/C_f. Expt. SDI-2
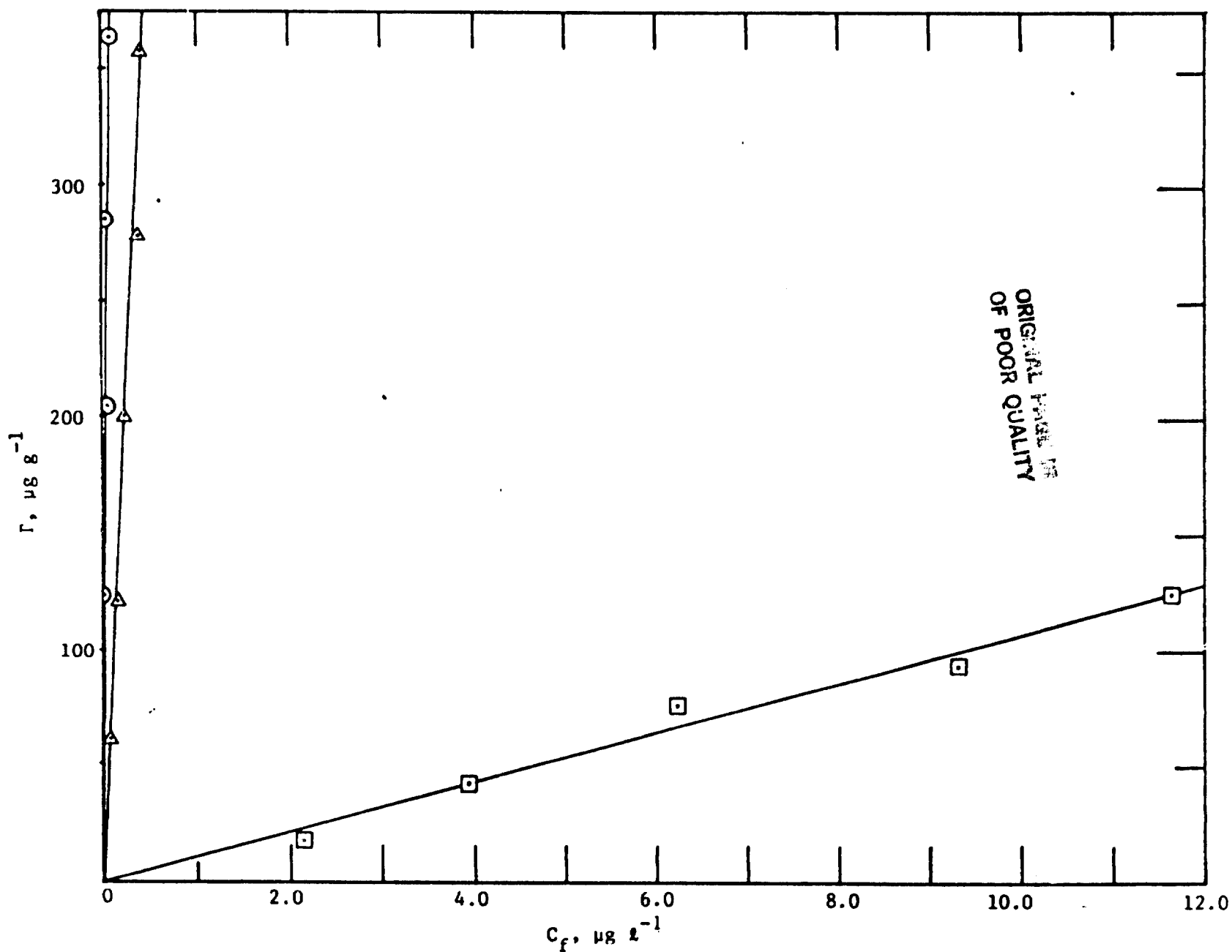
Figure 21: Adsorption Isotherm of Cadmium at 35°C. Plot of Surface Concentration, Γ, Against Free Cadmium, C_f, at Equilibrium.

(o) Expt. Cd1; ($\triangle$) Expt. Cd2; ($\square$) Expt. Cd3